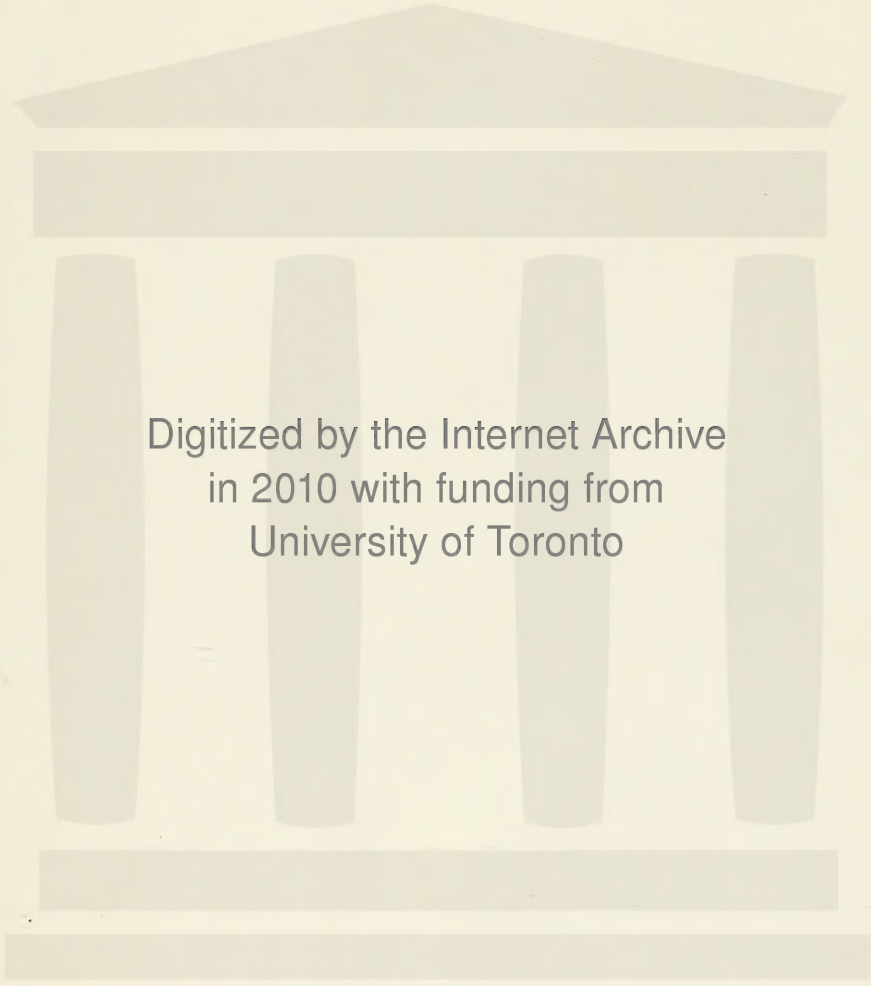

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The Journal of Industrial and Engineering Chemistry

PUBLISHED BY

The American Chemical Society

EASTON, PA.

VOL. IV, 1912

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CONTENTS

JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY

VOL. IV, 1912

JANUARY.

TORIALS:

Some Applications of Wrought Tungsten and Molybdenum.. 2
"The Fellow Who Doesn't Know Any Better"..... 4

GINAL PAPERS:

Deterioration and Spontaneous Heating of Coal in Storage. By Horace C. Porter and F. K. Ovitz..... 5
The Distillation of Alcohol. By A. B. Adams, Chief Chemist, Internal Revenue Bureau..... 8
Pure Linseed Oil. By E. J. Sheppard..... 14
Arsenic in Glass. By S. R. Scholes..... 16
The Determination of Chromium and Its Separation from Vanadium in Steels. By J. R. Cain..... 17
The Bismuthate Method for Manganese. By D. J. Demorest.. 19
Salt-Rising Bread and Some Comparisons with Bread Made with Yeast. By Henry A. Kohman..... 20
A Rapid Method for the Determination of Sulphur in Roasted Blende. By C. C. Nitchie..... 30
Jamaica Camphor. By H. W Emerson and E. R. Weidlein... 33
The Index of Refraction of the Mixed Acids of Fatty Oils. By W. B. Smith..... 36
The Chlorine Content of Milk. By Paul Poetschke..... 3
Temperature Corrections in Raw Sugar Polarizations. By W. D. Horne..... 41

ORATORY AND PLANT:

An Electric Laboratory Furnace. By Raymond C. Benner... 43
A Still for Absolute Alcohol. By Ralph H. McKee..... 46
An Automatic Pipette. By T. O. Smith..... 47
A New Melting-Point Apparatus. By D. S. Pratt..... 47

RESSES:

Address at the Unveiling of the Bust of Wolcott Gibbs. By Charles E. Munroe..... 48
Chemical Industries in Sweden. By Thomas H. Norton..... 51
Fuel Economy in Factories. By C. E. Lucke..... 58

Deflocculation. By Edward C. Acheson..... 62
The Chemist and the Cotton Seed Oil Industry in America. By David Wesson..... 64

NOTES AND CORRESPONDENCE:

Correction: The Preparation and Properties of Metallic Cerium 65
The Méker Burner..... 66
Imports and Exports of Farmers' Materials..... 66
What Our Rivers Carry..... 67
Cement Production to 1910..... 67
World's Production of Coal..... 67
The Mineral Production in North Carolina during 1908–10.... 68
Chief Geologist, Geological Survey..... 68
Nation's Coal Production..... 68
Cuba Iron-Ore Production..... 68
Greatest Iron-Producing Region in the World..... 68
Illinois Coal Production..... 68
Coal Exports in 1910..... 68
Oil in Alaska..... 69
Pure Food and Drug Law in Montana..... 69
Bureau of Mines Appropriations..... 69
Civil Service Examination..... 69

BOOK REVIEWS:

Handboek ten Dienste van de Suikerriet-Cultur en de Reitsuikerfabricage op Java; The Manufacture of Sulphuric Acid and Alkali; Die Metallurgie des Wolframs mit besonderer Beruecksichtigung der Elektrometallurgie; Annual Tables of Constants and Numerical Data (Chemical, Physical and Technological)..... 69

NEW PUBLICATIONS..... 70

RECENT INVENTIONS..... 72

MARKET REPORT..... 74

FEBRUARY.

TORIALS:

Potash from the Pacific Kelps..... 76
Surface Combustion..... 77
Physical-Industrial Chemistry..... 79

GINAL PAPERS:

Some Problems in Chemical Engineering Practice. Manufacture and Testing of Shipping Cylinders for Anhydrous Ammonia. By F. W. Frerichs..... 80
The Manufacture and Testing of Carbonic Acid Cylinders. By John C. Minor, Jr..... 88
The Composition of Some Mine Gases, and a Description of a Simple Methane Apparatus. By G. A. Burrell..... 96
Salt-Rising Bread and Some Comparisons with Bread Made with Yeast. By Henry A. Kohman..... 100
A Study of the Viscosity of Fish Oils. By George F. White... 106

ORATORY AND PLANT:

Hardness of Plasters and Cements, and a Simple Chronographic Apparatus for Recording Set. By Chas. F. McKenna.. 110
Recent Improvements in Filtration Methods. By Ernst J. Sweetland..... 114
An Electric Still Adapted for Difficult Distillations. By I. C. Allen and W. A. Jacobs..... 118
The Carbon Dioxide Recorder as a Factor in Fuel Economy. By E. A. Uehling..... 123

RESSES:

Mineral Wastes: The Chemists' Opportunity. By Chas. L. Parsons..... 125

KIN MEDAL AWARD:

Introduction. By M. C. Whitaker..... 131
Presentation Address. By C. F. Chandler..... 132
Address of Acceptance. By Herman Frasch..... 134

Geology of the Sulphur and Sulphur Oil Deposits of the Coastal Plain. By Captain A. F. Lucas..... 140
Sulphur Mines of the Union Sulphur Company in Louisiana. By F. H. Pough..... 143

SCIENTIFIC SOCIETIES:

Forty-fifth Annual Meeting A. C. S. Program of Papers..... 147
Minutes of Division of Industrial Chemists and Chemical Engineers..... 148
Minutes of Division of Agriculture and Food Chemistry..... 149
Minutes of the Division of Pharmaceutical Chemistry..... 150
Minutes of Meeting of Fertilizer Division..... 151
Minutes of the Meeting of the Rubber Section..... 152

NOTES AND CORRESPONDENCE:

Note on the Production of Mercury Fulminate. By Charles E. Munroe..... 152
Tungsten Production in the United States in 1911..... 153
Clay Products in 1910..... 153
Lead Industry in 1910..... 153

CONSULAR AND TRADE NOTES:

German Potash Interests..... 154
Norwegian Guano Shipments to United States..... 154
Glass Paving Blocks in France..... 154
Palm-Oil Industry of West Africa..... 154
Increased Custom Duties in Bolivia..... 154

BOOK REVIEWS:

Addresses to Engineering Students; Die Polarimetric der Erdöle. 155

NEW PUBLICATIONS..... 156

RECENT INVENTIONS..... 157

MARKET REPORT..... 158

MARCH.

EDITORIALS:

Conservation ... 160

MINERAL WASTES SYMPOSIUM:

Carbon Wastes. By J. A. Holmes ... 160
Zinc Losses. By W. H. Bassett ... 164
Need of Special Alloys for Special Purposes. By W. H. Bassett. 167
Waste and Conservation of Potash and Phosphoric Acid. By F. K. Cameron ... 169
Losses of Combined Nitrogen. By John D. Pennock ... 172
The Abuse of Brand. By A. D. Little ... 178
The Relation of the Silicate Industries to Conservation. By A. V. Bleininger ... 180
New Uses to Reduce Abuses in Conservation. By W. R. Whitney ... 182
Mineral Losses in Gases and Fumes. By F. G. Cottrell ... 182
Miscellaneous Mineral Wastes. By Chas. L. Parsons ... 185

ORIGINAL PAPERS:

A New Method for Testing Paint Films and Preservative Coatings for Iron and Steel. By W. C. Slade ... 189
A Short Method for the Determination of Soluble Arsenic in Commercial Lead Arsenates. By B. E. Curry and T. O. Smith ... 198
Valuation of Fluorspar. By E. Bidtel ... 201
Determination of Manganese in Steel. By James J. Boyle ... 202
Carbon Dioxide: Its Volumetric Determination. By Leon T. Bowser ... 203
The Value of the Higher Phenols in Wood-Preserving Oils. By Samuel Cabot ... 206
Composition of Dry Gluten and its Relation to the Protein Content of Flour. By Geo. A. Olson ... 206
A Comparative Study of Methods for the Determination of Hard and Total Soft Resins in the Hop. By H. V. Tartar and C. E. Bradley ... 209
The Chemistry of Anaesthetics, IV: Chloroform. By Charles Baskerville and W. A. Hamor ... 212

LABORATORY AND PLANT:

A Modified Wiley Extraction Apparatus. By W. D. Richardson and E. F. Scherubel ... 220
A Substitute for the Blast Lamp. By W. A. Ernst ... 221
A Convenient Filtering Apparatus. By G. S. Williams, Jr. ... 222
An Improvement on the Kjeldahl Distilling Apparatus. By W. L. Hadlock ... 222

COMMITTEE REPORTS:

Committee on Fertilizer Legislation. Fertilizer Division ... 223
Committee on Potash. Fertilizer Division ... 224
Committee on Phosphate Rock. Fertilizer Division ... 225
Committee on Nitrogen. Fertilizer Division ... 225
Committee on Standard Specifications and Methods for Analysis. Industrial Division ... 225
Committee on Definition of Industrial Terms. Industrial Division ... 226
Committee on Professional Code of Ethics. Industrial Division ... 226

NOTES AND CORRESPONDENCE:

A Note on Sampling. By W. J. Sharwood ... 227
Laboratory Preparation of Litmus Paper ... 229
Perilla Oil ... 229
Barleys Exhibited at the Second International Barley and Hop Prize Exhibit ... 230
Eighth International Congress Notes ... 230

OBITUARIES:

Dr. Naokichi Matsui ... 230

CONSULAR AND TRADE NOTES:

German Bronze-Powder Industry ... 231
Electrolytic Recovery of Zinc ... 231
Sulphur Mines in Mexico ... 232
Amalgamation of British Cement Companies ... 232
Argentina's Wine Industry ... 232
Petroleum Output of the World ... 232
Oil from Sunflower Seed ... 232
Gas Production and Consumption in England ... 232

BOOK REVIEWS:

Some Chemical Problems of To-day; The Manufacture of Chemical Manures; The Technical Analysis of Brass and the Non-ferrous Alloys; Pure Foods. Their Adulteration, Nutritive Value and Cost; Plant Food. Its Sources, Conservation, Preparation and Application ... 233

NEW PUBLICATIONS ... 233

RECENT INVENTIONS ... 236

MARKET REPORT ... 238

APRIL.

EDITORIALS:

The Purification and Softening of Water by Permutite ... 240
The Paint and Varnish Industry of the United States ... 241

ORIGINAL PAPERS:

Carbon Brushes. By W. R. Whitney ... 242
The Relation of the Refractive Index of Soda Lime Glasses to Their Chemical Composition. By Edwin Ward Tillotson, Jr. ... 246
A New Method for the Determination of Vanadium. By D. J. Demorest ... 249
A Rapid Method for the Determination of Vanadium in Steels, Ores, etc., Based on its Quantitative Inclusion by the Phosphomolybdate Precipitate. By J. R. Cain and J. C. Hostetter ... 250
A New Method for the Determination of Vanadium; an Explanation. By J. R. Cain and D. J. Demorest ... 256
The Rapid Determination of Vanadium in Steel. By Frank Garratt ... 256
The Direct Determination of Small Amounts of Platinum in Ores and Bullion. By Frederic P. Dewey ... 257
The Determination of Moisture in Coals. By E. H. Archibald and J. N. Lawrence ... 258
A Method for the Utilization of Lead Furnace Fume. By L. S. Hughes ... 262
A Method for Testing Out Problems in Acid Phosphate Manufacture. By F. B. Porter ... 264
On the Determination of Carbon Dioxide in Soils. By Leon T. Bowser ... 265
The Phenomenon of the Apparent Disappearance of the Higher Boiling Phenols in Creosoted Wood and its Explanation. By Samuel Cabot ... 266
The Fluidity of Fish Oil Mixtures as an Additive Property. By George F. White ... 267
Comparative Value of Irrigated and Dry-Farming Wheat for Flour Production. By Robert Stewart and C. T. Hirst. 270
The Influence of Carbon upon Nitrification. By H. W. Clark and George O. Adams ... 272
Acidity in Wheat Flour; its Relation to Phosphorus and to other Constituents. By C. O. Swanson ... 274
The Chemistry of Anaesthetics, IV: Chloroform. By Charles Baskerville and W. A. Hamor ... 278

LABORATORY AND PLANT:

The Adaption of the Centrifugal Pump to Chemical Problems. By F. G. Wheeler ... 288
New Forms of Gas Analysis Apparatus. By G. A. Burrell ... 297
An Improved Extraction Apparatus. By W. C. Blasdale ... 302
Notes on a New Form of Extraction Thimble. By P. A. Boeck ... 303

ADDRESSES:

Fertilizer Chemistry—A Report of Progress. By Paul Rudnick ... 304

CURRENT INDUSTRIAL NEWS:

Progress of the Chemistry of Papermaking ... 307
Recent Investigations on Alloys ... 307
Siloxide ... 308
Extraction with Naphthalene ... 308
Fire Extinction ... 309

TES AND CORRESPONDENCE:

The Centenary of the Introduction of Gas ... 309
American Electrochemical Society, Twenty-first General Meeting, Boston, April 18th to 20th ... 309
American Commission on Organic Nomenclature ... 309
Eighth International Congress of Applied Chemistry ... 310
Correction. A Convenient Filtering Apparatus ... 310
The Business Aspect of the Kelp Proposition. By Frederick P. Dewey ... 311
Importations of Acetic Anhydride ... 311

NSULAR AND TRADE NOTES:

English Municipal Gas Works ... 312
Utilization of Natural Gas in Hungary ... 312
Swedish Coal Situation ... 312
Cork Trade of the United States ... 312
Malaysian Tin Exports ... 312
Shark's Liver Oil Industry Proposed ... 312

BOOK REVIEWS:

Transactions of the American Institute of Chemical Engineers; The Technology of Bread-Making, Including the Chemistry and Analytical and Practical Testing of Wheat, Flour and other Materials Employed in Bread-making and Confectionery; Die Chemie der trocknenden Oele ... 313

NEW PUBLICATIONS ... 314

RECENT INVENTIONS ... 315

MARKET REPORT ... 316

MAY.

ITORIALS:

The United States Patent System ... 318

TENT SYMPOSIUM:

The Inventor, the Public and the Law. By Walter F. Rogers. 320
Patents and Chemical Industry in the United States. By B. Herstein ... 328
The Abuses of Our Patent System. By L. H. Baekeland ... 333

IGINAL PAPERS:

Some Recent Developments in Wood Distillation. By Thos. W. Pritchard ... 338
The Manufacture of Chloroform from Bleaching Powder and Ethyl Alcohol. By F. W. Frerichs ... 345
The Causes for Variations in Volatile Matter Determinations. By S. W. Parr ... 352
Monel Metal. By Richard H. Gaines ... 354
Free Lime in Portland Cement. By H. E. Kiefer ... 358
The Chemistry of Anaesthetics, IV: Chloroform. By Charles Baskerville and W. A. Hamor ... 362
Testing Methods of Rubber Contents in Raw and Vulcanized Rubber. By W. A. Ducca ... 372
The Volatile Acidity of Gum Tragacanth Compared with that of Indian Gum. By W. O. Emery ... 374
The Extraction of Potash and Alumina from Feldspar. By H. W. Foote and S. R. Scholes ... 377
A Colorimetric Method for the Determination of Carbon in Iron and Steel. By Jerome F. Kohout ... 378

BORATORY AND PLANT:

The Distribution of Power in Portland Cement Manufacture. By Richard K. Meade ... 378
New Forms of Apparatus for Gas Analysis. By F. M. Williams. 380

RRENT INDUSTRIAL NEWS:

Tannery Wastes in Sewage ... 382
Scientific Methods for Earthenware Manufacture ... 383
The Decolorization of Sugar Juice with "Eponite" ... 383
The Prevention of Iron and Steel Corrosion ... 383
Lohmannizing ... 384
The Influence of Additions to Bronze ... 384
Copper Fungicides ... 384
The Utilization of the Potassium Content of Minerals ... 384
Purification of Water by Forced Oxidation ... 384
The "Chloride" Water Purification Process ... 385
The Serpek Process of Nitrogen Fixation ... 385
Diastafor in the Textile Industry ... 385
Wood Preserving ... 385
A New Filtering Material for Alkaline Liquids ... 385
Pumps ... 385
"Ratisal," a Trap Substitute ... 386
A Dry Fire Extinguisher for Electric Installations ... 386
A New Pattern in Spray Nozzles ... 386
The Digby and Biggs Dionic Water Tester ... 386
New Tank Valve ... 386

NOTES AND CORRESPONDENCE:

The Paint and Varnish Industry ... 387
Determination of Manganese in Steel. A Note ... 387
Apocynum or Indian Hemp, Rubber. By Charles P. Fox. 387
Natural Gas ... 388
Natural Cement *versus* Portland Cement ... 388
Electric Production of Ferro-Tungsten ... 388
Bureau of Standards Analyzed Samples ... 388

BOOK REVIEWS:

"Rubber;" Paint Technology and Tests; Chemicals, Oils and Paints; Circular on Regulations for Illuminating Gas; Metallurgy of Iron and Steel; Casein, its Preparation and Technical Utilization ... 389

NEW PUBLICATIONS ... 391

RECENT INVENTIONS ... 393

MARKET REPORT ... 394

JUNE.

ITORIALS:

The Scope of Pharmaceutical Chemistry ... 396

IGINAL PAPERS:

Structure of Galvanized Iron. By Walter Arthur and William H. Walker ... 397
The Estimation of Oxygen and Occluded Gases in Copper and a Correction to the Electrolytic Assay in the Complete Analysis of Copper. By George L. Heath ... 402
Some Observations on the Disintegration of Cinder Concrete. By George Borrowman ... 405
The Manufacture of Chloroform from Bleaching Powder and Ethyl Alcohol. By F. W. Frerichs ... 406
Comparison of Some Methods for the Estimation of Sulphur in Vulcanized Rubber with Especial Reference to Electrolytic Oxidation. By D. Spence and J. Young ... 413
A Method for Determining the Value of Commercial Starches for Use in Cotton Mills. By G. M. MacNider ... 417
The Chemistry of Anaesthetics, IV: Chloroform. By Charles Baskerville and W. A. Hamor ... 422
Some Data on the Manufacture of Smoking Opium and Its Chemical Composition. By A. B. Adams and James M. Doran ... 429
The Composition of the Pacific Kelps. By J. W. Turrentine ... 432
A Note on the Determination of Iodides by Direct Titration. By J. W. Turrentine ... 435
Determination of Total Potassium in Minerals. By Charles J. Schollenberger ... 436
Note on the Neutral Permanganate Method for the Availability of Organic Nitrogen. By John Phillips Street ... 437
Activity of Organic Nitrogen as Measured by the Alkaline Permanganate Method. By C. H. Jones ... 438
The Effect of the "Wet Process" on the Availability of Low-Grade Nitrogenous Materials. By Burt L. Hartwell and F. R. Pember ... 441
Neutral Ammonium Citrate Solution. By A. J. Patten and C. S. Robinson ... 443

LABORATORY AND PLANT:

The Manufacture of Gelatine. By Ludwig A. Thiele ... 446
A Punch for Straight Rubber Test Pieces. By Harry P. Mills. 452
A Laboratory Generator for Hydrochloric Acid Gas. By Edwin Dowzard ... 452
Two Pieces of Laboratory Apparatus. By Harold Canning Chapin ... 453
Unique Water Bath. By S. W. Wiley ... 454

ADDRESSES

Occupational Poisoning in Chemical Trades. By W. Gilman Thompson ... 454
The Progress of the Work on the Revision of the United States Pharmacopoeia. By H. P. Remington ... 457

CURRENT INDUSTRIAL NEWS

The Industrial Uses of Ozone ... 459
Non Freezing Mixtures ... 460
A New Liquid Mixer ... 460
The Sterilization of Potable Waters ... 461
Portland Cement ... 461
Bleaching Powder as a Soap Substitute ... 416
Water Gauge Glasses ... 461
Packing in Steam Plants ... 461
Developments in Steam Generation ... 462
The Contact Process of Sulphuric Acid Manufacture ... 462
Fortoline ... 462
The Utilization of Storage Battery Sludge ... 462
The Manufacture of White Lead ... 462
The Purity of Commercial Metals ... 462
The Cost of Chlorine ... 463
Synthetic Organic Dyes and Patents for the Manufacture of the Same, 1907-'11 ... 463
The Manufacture of Aluminum Foil ... 463
Some New "Non-Corrosive" Alloys ... 463
Kupronizing ... 463

NOTES AND CORRESPONDENCE

The German Patent System ... 464
Originality of Inventions ... 465
Report of the Delegate to the Joint Conference of the Patent System ... 466
Report of the Committee on Quantitative Methods ... 467
The Technical Analysis of Brass and the Non Ferrous Alloys: Author's Note ... 469
Volatility of Metals of the Platinum Group ... 470
Chemistry and the Lithographic Industry ... 470
Contamination of Laboratory Samples by Iron Derived from Crushing Machinery ... 471
Combating Miners' Diseases ... 471

BOOK REVIEWS

Strength of Materials, Fertilizer and Fertilizer Hints, Die Chemie der Cellulose with Particular Reference to the Textile and Cellulose Industries; Chemiker Kalender; The Manufacture of Varnishes, and Kindred Industries; Technical Methods of Chemical Analysis; Cocoa and Chocolate, Their Chemistry and Manufacture; A Manual of Fire Assaying ... 471

NEW PUBLICATIONS ... 474

RECENT INVENTIONS ... 475

MARKET REPORT ... 476

EDITORIALS:

The Production of Ethyl Alcohol from Waste Products ... 478
Occupational Diseases ... 480

ORIGINAL PAPERS:

Corrosion of Iron in Pure Water and Air Combined; the Electrolytic Theory again Confirmed. By William R. Fleming ... 480
The Relative Corrosion of Iron and Steel Pipe as Found in Service. By William H. Walker ... 486
Description of the Explosion Test at the Experimental Mine of the United States Bureau of Mines, February 24, 1912. By George S. Rice ... 488
The Expansion Coefficient of Graphite. By Arthur L. Day and Robert B. Sosman ... 490
A Volumetric Method for the Determination of Thorium in the Presence of Other Rare Earths. The Analysis of Monazite Sand. By F. J. Metzger and F. W. Zons ... 493
The Resenes of Resins and Oleoresins. By Charles H. Herty and W. S. Dickson ... 495
A Method of Examining China Wood Oil. By Parker C. McIlhiney ... 496
On the Indices of Refraction of China Wood Oil. By Louis Elsberg Wise ... 497
The Refractive Index of Beeswax. By L. Feldstein ... 498
The Chemistry of Anaesthetics, IV: Chloroform. By Charles Baskerville and W. A. Hamor ... 499
Laboratory Studies of Rennin. By A. Zimmermann ... 506
Micro-Chemical Tests for the Identification of Some of the Alkaloids. By Earl B. Putt ... 508
An Improved Method of Assay for Aromatic Sulphuric Acid. By Linwood A. Brown ... 512
A Method for Assaying Spirits of Camphor. By Arthur T. Collins ... 514
Suggested Modifications to the U. S. P. Assay of Opium. By R. Norris Shreve ... 514
A Note on the Determination of the Digestive Value of Papain. By J. R. Rippetoe ... 517
The Bromine and Iodometric Methods for the Volumetric Determination of Cresol. By C. M. Pence ... 518
The Accurate Volumetric Determination of Phosphoric Acid in Phosphate Rock. By John G. Fairchild ... 520
The Determination of Total Manganese in Soils. By Ross A. Gortner and Clayton O. Rost ... 522
Altering the Composition of Indian Corn by Seed Selection. By L. H. Smith ... 524
Relation of Active Potash to Pot Experiments. By G. S. Fraps ... 525
The Detection of Formic Acid in Fruit Products. By F. L. Shannon ... 526
The Detection of Prussian Blue in Tea. By Fred West ... 528

LABORATORY AND PLANT:

Factors Determining the Capacity of a Filter Press. By C. Almy, Jr., and W. K. Lewis ... 528
Improved Sulphuric Acid Chambers. By Thomas H. Norton. 532

JULY.

A Modification of the Frary Electrodynamic Stirring Device. By J. M. Knote and W. R. Work ... 534
The Underwriters' Laboratories Extraction Apparatus. By Henry J. Cary-Curr ... 535

ADDRESSES:

The Present Status of the Gas Industry and Its Outlook. By Charles E. Munroe ... 536

CURRENT INDUSTRIAL NEWS:

Selenium Glass ... 539
Heavy Oil Engines ... 540
The Classification of Soaps ... 541
The Spontaneous Combustion of Charcoal ... 541
Artificial Rubber from Seaweed ... 542
"Tempered Copper" Tools ... 542
The Purification of Air by Ozone ... 542
The Use of Coke-Oven Gas ... 542
The Preservation of Wood with "Bellit" ... 542
Chrome-Nickel Bronze ... 542

NOTES AND CORRESPONDENCE:

Notes on the Composition and Analysis of Desiccated Milk and Cream ... 543
A Modification of the Babcock Test as Applied to the Estimation of Fat in Desiccated Milk ... 544
Alundum not Constant in Weight ... 544
The Centenary of the Introduction of Gas ... 545
American Electrochemical Society Research Fund ... 546
Maine Section of the American Chemical Society ... 546
Organization of Committees for Study of Industrial Diseases ... 547
Organization of Rubber Section ... 547
Paint and Varnish in the U. S. Navy ... 547
A Colorimetric Method for the Determination of Carbon in Iron and Steel. A Note of Protest ... 547
A Colorimetric Method for the Determination of Carbon in Iron and Steel. A Note ... 548
Valuation of Fluorspar—A Correction ... 548
General Bakelite Company Starts Infringement Suits ... 548
The End of the Coöperative Glass Factories in Italy ... 548
International Congress of Applied Chemistry. Announcement of Section I, Analytical Chemistry ... 548

BOOK REVIEWS:

Corrosion of Iron and Steel; Technologic Papers of the Bureau of Standards, No. 3; Tests of the Absorptive and Permeable Properties of Portland Cement Mortars and Concretes, together with Tests of Damp-proofing and Waterproofing Compounds and Materials; A Dictionary of Applied Chemistry; Allen's Commercial Organic Analysis; The Chemistry of Breadmaking; The Laboratory Apparatus Blue Book ... 549

NEW PUBLICATIONS ... 551

RECENT INVENTIONS ... 552

MARKET REPORT ... 554

AUGUST.

ORIALS

The Eighth International Congress of Applied Chemistry . . 556

GINAL PAPERS:

The Manufacture of Carbon Bisulphide. By Edward R. Taylor . . . 557
The Occurrence of Efflorescence on Lava Bricks. By William McGeorge . . . 559
Enamels for Sheet Steel. By Robert D. Landrum . . 561
The Production of Excessive Hydrogen Sulphide in Sewage Disposal Plants and Consequent Disintegration of the Concrete. By William M. Barr and R. E. Buchanan . . 564
Marking Porcelain and Silica Crucibles, etc. By P. A. Yoder . . 567
On the Quantitative Estimation of Sodium Hydroxide in "Black Liquor." By Edwin Sutermeister and Harold R. Rafsky . . . 568
The Chemistry of Anaesthetics, IV Chloroform. By Charles Baskerville and W. A. Hamor . . . 571
On the Starch of Glutinous Rice and its Hydrolysis by Diastase. By Yoshio Tanaka . . . 578
The Effect of Sulphurous Acid on Fermentation Organisms. By W. V. Cruess . . . 581
Concerning the Sugar Content of Watermelons. By Carl P. Sherwin and Clarence E. May . . . 585
The Determination of Benzaldehyde on Maraschino Cherries and Maraschino Liqueur. By A. G. Woodman and Lewis Davis . . . 588
Commercial Cinnamon and Cassia. By Harry E. Sindall . . . 590
The Ripening of Hops. By C. E. Bradley and H. V. Tartar . . 591
Analysis of Some Fats of the American Buffalo (Bison). By Robert H. Smith . . . 592
The Determination of Eucalyptol (Cineol) in Essential Oils. By Francis D. Dodge . . . 592
Recent Analyses of the Saratoga Mineral Waters. By Leslie Russell Milford . . . 593
Determination of Lithium. By Leslie Russell Milford . . . 595
A New Volumetric Method for Tin. By Wilbur W. Patrick and G. C. Wilsnack . . . 597
A New Apparatus for the Volumetric Determination of Carbon Dioxide. By Howard W. Brubaker . . . 599
A Modification of the Sweeney Method for Crude Fiber. By Cornelia Kennedy . . . 600
Studies on Soil Humus. By Sherman Leavitt . . . 601
An Examination of City Street Sweepings. By J. J. Skinner and J. H. Beattie . . . 604
Inorganic Phosphorus in Plant Substances A Method of Estimation. By R. C. Collison . . . 606

ORATORY AND PLANT:

Design and Equipment of the Chemical Engineering Laboratory at the University of Washington. By H. K. Benson . . . 609
A New Apparatus for the Determination of Carbon Dioxide. By E. W. Gaither . . . 611
Automatic Filter Feed. By Thos. A. Mitchell . . . 613
Note on Protectors for Glass Stopcocks. By Walter O. Snelling . . . 613
Alundum Crucibles in Gravimetric Analysis. By Guilford L. Spencer . . . 614

ADDRESSES

Natural Gas Investigations of the Bureau of Mines. By George A. Burrell . . . 614
A Plan for the Support of Chemical Research and for the Better Teaching of Industrial Chemistry. By John Stewart . . . 616

CURRENT INDUSTRIAL NEWS:

The Manufacture of Nitrates from the Atmosphere . . . 619
A Process for the Fixation of Atmospheric Nitrogen . . . 619
The Corrosion of Iron and Steel . . . 619
Uses of Aluminum . . . 620
Briquetting Metallic Waste . . . 620
The Revival of the Kelp Industry . . . 620
Lighting by Neon Tubes . . . 620
"Granacit" . . . 621
The Destructive Action of Acids on Concrete . . . 621
"Ironizing," or "Ferrozincing" . . . 621
A New Process for Electro-Zincing . . . 621
Textilose . . . 621
The Bleaching of Linen . . . 621
Phosphorus Slag as an Insecticide . . . 621
Oxygen Additions to Iron Furnace Blast . . . 622
New Composite Sheet Metals . . . 622
A New Use for Boron . . . 622
Vanadium Babbitt Metal . . . 622
A New Vacuum Gauge . . . 622
A New Form of Valve for Gas Cylinders . . . 622
The Measurement of Steam Consumption . . . 623
A New Joint for Steel Pipe . . . 623

NOTES AND CORRESPONDENCE:

Sea-weed, Potash and Iodine. A Criticism . . . 623
Nigerian Tin Developments . . . 624
The Oil of Pochote . . . 625
Lectures on the Smoke Problem . . . 626
Detection of Formaldehyde in Foods . . . 626
Laboratory Generator for Hydrochloric Acid Gas . . . 626

BOOK REVIEWS:

An Introduction to the Study of Fuel; Annual Tables of Constants and Numerical Data; Chemical, Physical and Technological; The Chemistry of the Radio Elements; The Chemistry of the Rubber Industry; German Varnish Making; Industrial Organic Chemistry; Vinegars and Catsup, Interpretation of Standards, Analyses, Etc . . . 626

NEW PUBLICATIONS . . . 628

RECENT INVENTIONS . . . 629

MARKET REPORT . . . 632

SEPTEMBER.

TORIALS

Our Guests . . . 634
Fussy Administration . . . 634

GINAL PAPERS

Epinephrin from the Whale. By Edward R. Weidlein . . . 636
The Chlorides of Carbon as Solvents, I: Carbon Tetrachloride. By Charles Baskerville and H. S. Riederer . . . 645
On the Surface Tension of Silicate and Borosilicate Glasses. By Edwin Ward Tillotson, Jr. . . . 651
The Detection and Determination of Cyanogen and Hydrogen Cyanide. By F. H. Rhodes . . . 652
Rapid and Accurate Methods for Determining Phenol By L. V. Redman and E. O. Rhodes . . . 655
The Colorimetric Determination of Iron in Lead and its Oxides. By John A. Schaeffer . . . 659
A Rapid Microscopical Method for the Determination of Arsenic, as Orpiment, in Shellac. By Robert Schwarz. 660
Some Practical Methods for Testing and Identifying Colors for Printing Inks and Similar Pigments. By Samuel Levinson . . . 661
The Effect of Ignition on the Solubility of Soil Phosphates. By Chas. B. Lipman . . . 663
The Determination of Humus in Hawaiian Soil. By W. P. Kelley and Wm. McGeorge . . . 664
The Composition of Fusel Oil from Beet Molasses. By M. C. Boswell and J. I. Gooderham . . . 667
Difficulties in the Colorimetric Estimation of Vanillin. By W. S. Hubbard . . . 669
A New Colorimetric Method for the Determination of Vanillin in Flavoring Extracts By Otto Folin and W. Denis . . . 670
Method for Determining Fat in Sugared Evaporated Milk. By F. C. Broeman . . . 672

LABORATORY AND PLANT

A New Type of Inorganic Filter for Laboratory Purposes. By M. A. Williamson and P. A. Boeck . . . 672
Calculation of Sulphuric Acid Stock by Approximate as Accurate Methods A Special Slide Rule for This Purpose By H. C. Moore . . . 677
A Simple and Inexpensive Conductivity Cell. By Carl A. Nowak . . . 679

Apparatus for Funneless Kjeldahl Nitrogen Digestion. By A. P. Sy ... 680
A Simple Method for Purifying Drinking Water. By J. L. Simmis ... 681
Sampling Cone. By C. W. Knefl ... 682
A Laboratory Glass Furnace. By S. R. Scholes ... 683
The Determination of Carbon in Steel by Direct Combustion in the Newest Form of Shimer Crucible, with the Aid of a Perforated Clay Disc. By Frank O. Kichline ... 683
A Modified Victor Meyer Apparatus. By Harold Canning Chapin ... 684

ADDRESSES:

The Analyst *versus* The Chemist. By J. S. Brogdon ... 684

CURRENT INDUSTRIAL NEWS:

Factory Inspection ... 686
Factory Ventilation ... 686
Mercury Poisoning ... 686
Specifications for Refractories ... 686
The Utilization of Sulphite Liquor ... 687
Italian Shipments of Carbon Disulphide ... 687
The Condition of the Chilean Saltpeter Industry ... 687
Methyl Chloride as a Refrigerating Agent ... 687
Accelerating Paint Drying with Ozonized Air ... 687
A New Process for Producing Stearic Acid ... 687
The Rapid Production of Pure Cream of Tartar ... 687
"Duriron" ... 688
Lead for Calking Joints ... 688
"Vanalium" ... 688
"Argilite" ... 688
A Water Flow Recorder ... 688
The Manufacture of Suction Hose ... 688
Heat Transmission in Vacuum Evaporator Tubes ... 689
A New Crude Oil Engine ... 689
A Double Oiling System Pump ... 689
Air Jet Chimney Ventilator ... 689
The Utilization of Peat ... 689

NOTES AND CORRESPONDENCE:

Seaweed, Potash and Iodine ... 690
Ordinary Writing Fluid for Marking Porcelain Crucibles ... 691
The Need of Chemical Control in Furnace Operation ... 691
The Estimation of Oxygen and Occluded Gases in Copper, Etc. Author's Note ... 691
Chemical Industries of Norway ... 691
Cement Production and Trade in the Far East ... 694
Sulphur, Pyrite, and Sulphuric Acid ... 695
Chemical Industry of Germany ... 695
German Potash and Salt Statistics ... 696
The Wide Use of Arsenic ... 696
Swiss Factory Statistics ... 697
Titanium and Alloys of Steel ... 697
Good Increase in Platinum Production ... 697
Paint Production in 1911 ... 697
Waste in Coke Making ... 697
Coal Exports in 1911 ... 698

BOOK REVIEWS:

Correction. Thorpe's Dictionary of Applied Chemistry; A Dictionary of Applied Chemistry; Portland Cement; The Cement Industry in 1911; Practical Chemistry for Engineering Students; Snap Commercial Analysis ... 698

NEW PUBLICATIONS ... 700

RECENT INVENTIONS ... 701

MARKET REPORT ... 704

OCTOBER.

INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY:

The Inaugural Meeting at Washington ... 707
The New York Meeting ... 711
The International Lectures ... 712
The Sectional Addresses ... 712
The Sectional Meetings ... 713
The Social Features of the Congress ... 713
The Closing Session ... 715
Factory Visits and Excursions ... 715
The Societies at the Congress ... 716

ORIGINAL PAPERS:

The Control of Dust in Portland Cement Manufacture by the Cottrell Precipitation Processes. By Walter A. Schmidt. 719
Contact Sulphuric Acid from Brimstone. By G. W. Patterson and L. B. Cheney ... 723
Smelter Smoke Conservation. By George C. Westby ... 725
Notes on a Study of the Temperature Gradients of Setting Portland Cement. By Allerton S. Cushman ... 728
Cobalt Driers. By V. P. Krauss ... 731
The Development of Hydrosulphites in Their Relation to Modern Dyestuffs. By Philip S. Clarkson ... 733
The Effect of "Lime-Sulphur" Spray Manufacture on the Eyesight. By James R. Withrow ... 735
Phenol-Formaldehyde Condensation Products. By L. H. Baekeland ... 735

LABORATORY AND PLANT:

Apparatus for the Examination and Study of the Behavior of Valve and Cylinder Oils and other Petroleum Lubricating Oils in Saturated and Superheated Steam, Carbon Dioxide, Air and Other Gases. By P. H. Conradson. 744
A New Calorimetric Bomb with Special Advantages as to Material of Construction and Method of Operation. By S. W. Parr ... 746
Some Tests on a New Calorimetric Bomb. By Richard H. Jesse, Jr. ... 748

ADDRESSES:

The Latest Achievements and Problems of the Chemical Industry. By Carl Duisberg ... 749
Synthetic Ammonia. By H. A. Bernthsen ... 760
Progress in Industrial Chemistry. By Rudolph Messel ... 767
Oxidation of Atmospheric Nitrogen and Development of Resulting Industries in Norway. By Samuel Eyde ... 771

CURRENT INDUSTRIAL NEWS:

A New Wood Preservative ... 774
Air Compressor Lubrication ... 774
The Oxygraph ... 775
The Manufacture of Lithopone ... 775
The Pollution of Streams by Spent Gas Liquor ... 776
The Melting Points of Fire Bricks ... 776
"Persil" as a Bleaching Agent ... 776
The Disinfection of Potable Waters by Chloride of Lime ... 777
Ammonia Evaporation and Transformation in Soils ... 777
The Location of Underground Pipes ... 777
The Casting of Magnesium Alloys ... 777

NOTES AND CORRESPONDENCE:

Obituary—Frederick J. Mayer ... 777
Third International Rubber Conference ... 778
Municipal Water Conservation Exhibit of the City of Philadelphia ... 778

NEW PUBLICATIONS ... 779

MARKET REPORT ... 782

NOVEMBER.

EDITORIALS:

Morris Loeb ... 784
The Incongruities of American Patent Litigation ... 785

ORIGINAL PAPERS:

Distillation of Resinous Wood by Saturated Steam. By L. F. Hawley and R. C. Palmer ... 789
The Determination of Oxygen in Iron and Steel by Reduction in an Electric Vacuum Furnace. By Wm. H. Walker and Walter A. Patrick ... 799
The Methods of the United States Steel Corporation for the Commercial Sampling and Analysis of Pig Iron. By the Chemists' Committee of the U. S. Steel Corporation ... 801
The Synthesis of Hydrocarbons at High Temperatures and Pressures. By J. N. Pring and D. M. Fairlie ... 812

Glass Formulas: A Criticism. By Alexander Silverman.... 818
On the Density of Some Borate and Silicate Glasses. By Edwin Ward Tillotson, Jr.... 820
Extraction of Thoria. By Charles Baskerville.... 821
The Production of Available Potash from the Natural Silicates. By Allerton S. Cushman and George W. Coggeshall.... 821
Potash, Silica and Alumina from Feldspar. By Edward Hart.... 827
Composition of the Salines of the United States. By J. W. Turrentine, with analyses by A. R. Merz and R. F. Gardner.... 828
The Determination of Phosphorus in Commercial Acetylene By L. M. Dennis and W. J. O'Brien.... 834
The Determination of Lead Sulphate and the Ultimate Estimation of Sublimed White Lead in Rubber. By John A. Schaeffer.... 836
The Effect of Kiln-Drying at 145° F. on the Composition of the Hop. By H. V. Tartar and B. Pilkington.... 839

LABORATORY AND PLANT:

Combination of the Contact Process with the Ordinary Lead Chamber or Tower Systems; an Improvement in the Manufacture of Sulphuric Acid. By William Wilke... 840
A Simple Test for the Determination of Butter-fat in Butter. By James M. Doran.... 841
Apparatus and Method for Sulphur Determination in Petroleum Illuminating and Lubricating Oils. By P. H. Conradson.... 842
Carbon Dioxide Absorption Bottle. By W. A. Koenig.... 844
A New Alloy with Acid Resisting Properties. By S. W. Parr. 844
Modified Bunsen Valve. By Leslie Russell Milford.... 845
A Simple Form of Laboratory Support. By T. Linsey Crossley.... 846

OBITUARIES:

Morris Loeb.... 846

CURRENT INDUSTRIAL NEWS:

Plumbism in New York City.... 849
The Chemical Industries of France in 1911.... 849
The Denaturation of Alcohol with Pyridine.... 850
The Status of the Artificial Silk Industry.... 850
Another Rubber Substitute.... 850
The State of the Platinum Market.... 850
Increasing the Resistance of Alloys to Chemical Action.... 851
The Purification of Boiler-feed Water.... 851
The Alkali Industry in Great Britain during 1911.... 851
Sulphur Dioxide from Iron Pyrites.... 852
A Hydrogen-supply for Dirigible Balloons.... 852
"Durobax" Glass.... 852
"Triplex" Glass.... 852
Imports and Exports of Chemicals.... 852
Acid-resisting Alloys.... 852
The Schoop Metallizing Process.... 853
The State of the Antimony Market.... 853
Porous Metals.... 853
Peat Fuel for the Production of Power.... 853
A New Water-jet Air-pump.... 854
The Parkinson Patent Furnace.... 854
Reinforced Galvanized Spiral Pipe.... 854
A New Automatic Water-Jet Air-Pump.... 854
The Use of Graphite in Boilers.... 855

NOTES AND CORRESPONDENCE:

The Third International Rubber Exhibition.... 855
The Underwriters' Laboratories Extraction Apparatus: A Note.... 856
Bureau of Standards Analyzed Samples.... 856
The Determination of Benzaldehyde, Maraschino Cherries and Maraschino Liqueur: A Correction.... 856
Phenol-formaldehyde Condensation Products: A Correction. 857

BOOK REVIEWS:

Industrial Chemistry; Foods and Drugs; Die Analyse der seltenen Erden und der Erdsuären; Researches in Cellulose; Methods of Organic Analysis.... 857

NEW PUBLICATIONS.... 859

RECENT INVENTIONS.... 860

MARKET REPORT.... 862

DECEMBER.

EDITORIALS:

The Research Corporation, an Experiment in Public Administration of Patent Rights.... 864

ORIGINAL PAPERS:

A Study of the Variations of the Physical and Chemical Properties of Red Lead. By O. W. Brown and A. R. Nees.. 867
The Continuous Purification of Coal Gas with Weak Ammonia Liquor. By J. G. O'Neill.... 876
Studies on Fish Oils, III: Properties of Fish and Vegetable Oil Mixtures. By George F. White and Adrian Thomas 878
The Relation of the Refractive Index of Soda-Barium and Soda-Lime Glasses to their Chemical Composition. By Edwin Ward Tillotson, Jr.... 882
The Composition of the Salines of the United States II. Natural (Subterranean) Brines and Mother Liquors from Natural Brines. By J. W. Turrentine, with Analyses by A. R. Merz and R. F. Gardner.... 885
The Determination of Zinc by Electroanalysis. By Ellwood B. Spear and Samuel S. Strahan.... 889
The Kambara Earth. A Decolorizing Material for Mineral Oils, etc By K. Kobayashi.... 891
Investigation of the Methods for the Determinations of Total Fatty Acids in Cotton-Seed Foots. By Frank N. Smalley.... 893
The Determination of Chromium and Vanadium in Steel. By D. J. Demorest.... 895
A Rapid Control Method for the Determination of Oil in Grains. By E. P. Harding and Lillian L. Nye.... 895
Soy Bean Cheese. By William V. Linder.... 897

LABORATORY AND PLANT:

A New Form of Orsat Apparatus. By L. M. Dennis.... 898
The Stormer Viscosimeter and the Value of Viscosity Determinations by its Use. By Gilbert Rigg and J. L. Carpenter.... 901
Apparatus and Method for "Carbon Test and Ash Residue" in Petroleum Lubricating Oils. By P. H. Conradson... 903
A Self-Filling Measuring Wash Bottle. By O. C. Smith.... 905

ADDRESSES:

A Plan for Organized Research and Analytical Chemistry in Successful Chemical Manufacturing. By William C. Ferguson.... 905
The Electrical Precipitation of Suspended Particles by the Cottrell Processes. By Linn Bradley.... 908
The Control of Temperature in the Operations of Analytical Chemistry By Theodore W. Richards.... 910

CURRENT INDUSTRIAL NEWS:

"Vitreosil" in the Nitric Acid Industry.... 913
Development of the Sulphite Industry.... 913
Problems in Papermaking.... 914
The Autumn Meeting of the Institute of Metals.... 914
Solid Oil as a Marine Fuel.... 915
High-Pressure Gas Lighting.... 915
The Properties of Motor Fuels.... 915
The Consumption of Oxygen.... 915
"Plumboxan".... 916
Aluminum Alloys.... 916
Metallurgie.... 916
A New Type of Continuous Furnace.... 916
Artificial Silks.... 916

NOTES AND CORRESPONDENCE:

Obituary—Thomas Price.... 917
A Suggestion Regarding the Graduation of Hydrometers.... 917
The Effect of "Lime-Sulphur" Spray Manufacture on the Eyesight.—A Note.... 917
The Andrew Carnegie Research Scholarship.... 917
American Institute of Chemical Engineers.... 918
The Chemical Societies in New York City.... 918
On the Starch of Glutinous Rice and its Hydrolysis by Diastase. —A Correction.... 918

BOOK REVIEWS:

Paper Pulps from Various Forest Woods, The Metallography of Iron and Steel: Analysis of Metallurgical and Engineering Materials.... 918

NEW PUBLICATIONS.... 920

RECENT INVENTIONS.... 921

MARKET REPORT.... 922

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume IV JANUARY, 1912 No. 1

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Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered at the Post-Office, Easton, Pa., as Second-class Matter.

TABLE OF CONTENTS.

EDITORIALS:

Some Applications of Wrought Tungsten and Molybdenum ... 2

"The Fellow Who Doesn't Know Any Better" ... 4

ORIGINAL PAPERS:

Deterioration and Spontaneous Heating of Coal in Storage. By Horace C. Porter and F. K. Ovitz ... 5

The Distillation of Alcohol. By A. B. Adams, Chief Chemist, Internal Revenue Bureau ... 8

Pure Linseed Oil. By E. J. Sheppard ... 14

Arsenic in Glass. By S. R. Scholes ... 16

The Determination of Chromium and Its Separation From Vanadium in Steels. By J. R. Cain ... 17

The Bismuthate Method for Manganese. By D. J. Demorest ... 19

Salt-Rising Bread and Some Comparisons with Bread Made with Yeast. By Henry A. Kohman ... 20

A Rapid Method for the Determination of Sulphur in Roasted Blende. By C. C. Nitchie ... 30

Jamaica Camphor. By H W. Emerson and E. R. Weidlein ... 33

The Index of Refraction of the Mixed Acids of Fatty Oils. By W. B. Smith ... 36

The Chlorine Content of Milk. By Paul Poetschke ... 38

Temperature Corrections in Raw Sugar Polarizations. By W. D. Horne ... 41

LABORATORY AND PLANT:

An Electric Laboratory Furnace. By Raymond C. Benner ... 43

A Still for Absolute Alcohol. By Ralph H. McKee ... 46

An Automatic Pipette. By T. O. Smith ... 47

A New Melting-Point Apparatus. By D. S. Pratt ... 47

ADDRESSES:

Address at the Unveiling of the Bust of Wolcott Gibbs. By Charles E. Munroe ... 48

Chemical Industries in Sweden. By Thomas H. Norton 51

Fuel Economy in Factories. By C. E. Lucke ... 58

Deflocculation. By Edward G. Acheson ... 62

The Chemist and the Cotton Seed Oil Industry in America. By David Wesson ... 64

NOTES AND CORRESPONDENCE:

Correction: The Preparation and Properties of Metallic Cerium ... 65

The Méker Burner ... 66

Imports and Exports of Farmers' Materials ... 66

What Our Rivers Carry ... 67

Cement Production to 1910 ... 67

World's Production of Coal ... 67

The Mineral Production in North Carolina during 1908–10 ... 68

Chief Geologist, Geological Survey ... 68

Nation's Coal Production ... 68

Cuba Iron-Ore Production ... 68

Greatest Iron-Producing Region in the World ... 68

Illinois Coal Production ... 68

Coal Exports in 1910 ... 68

Oil in Alaska ... 69

Pure Food and Drug Law in Montana ... 69

Bureau of Mines Appropriations ... 69

Civil Service Examination ... 69

BOOK REVIEWS:

Handboek ten Dienste van de Suikerriet-Cultur en de Reitsuikerfabricage op Java; The Manufacture of Sulphuric Acid and Alkali; Die Metallurgie des Wolframs mit besonderer Berucksichtigung der Elektrometallurgie; Annual Tables of Constants and Numerical Data (Chemical, Physical and Technological) 69

NEW PUBLICATIONS ... 70

RECENT INVENTIONS ... 72

MARKET REPORT ... 74

EDITORIALS

SOME APPLICATIONS OF WROUGHT TUNGSTEN AND MOLYBDENUM.

Only a few years ago a number of the elements were classed in the literature as brittle and had never been produced in a condition in which they were not brittle at room temperature, but have since been taken out of the brittle list. Among these are tungsten and molybdenum.

Prior to their production in ductile form, tungsten and molybdenum as such (that is, other than in alloys or compounds) had but one application, namely, in an incandescent lamp, the one as filament, and the other as filament support.

Some of the physical properties of these last-named industrially new elements, together with a rough sketch of the investigation work leading up to the production of ductile tungsten, have been published elsewhere (*Trans. Am. Electrochem. Soc.*, **17**, 229–234 (1910); *Proc. Am. Inst. E. E.*, **29**, Part II, 961–965 (1910)).

It is the purpose of this paper to tell of some of the applications which are being developed for wrought tungsten and wrought molybdenum. The writer presents it not only for the interest of the work itself, but also in the hope that it will stimulate work on the other so-called brittle metals, and it seems to him that some of our industries are almost certain to profit greatly by the discovery of each new ductile element.

THE DRAWN-WIRE TUNGSTEN INCANDESCENT LAMP.

A year and a half ago the hope was first publicly expressed that it would soon be possible to manufacture lamps on a large scale from ductile tungsten. This hope has been fulfilled, and the commercial development has been so rapid that already the bulk of the tungsten lamps made in this country are of drawn wire, and the manufacture is already established on a large scale in England and Germany. Some anxiety was at first felt lest it should not be possible to get diamond wire drawing dies of sufficiently small aperture to produce wire fine enough for the lowest candle power lamps which might be desired. But this fear proved groundless and wire is now produced in quantity down to 0.0006 inch in diameter.

Ductile molybdenum is used in some types of lamp as a support material for the tungsten filament.

THE TUNGSTEN OR MOLYBDENUM-WOUND FURNACE.

This has already been described by Winne and Dantsizen (THIS JOURNAL, 1911, p. 770), and has proved to be an exceedingly useful tool, especially so in connection with the production of wrought tungsten and molybdenum. Extensive factory use has shown it to be not only cheaper but, regardless of cost, far superior to a platinum-wound electric furnace. When wound on a body of alundum it permits of the attainment of higher temperature than can be reached with platinum. This attainment of the higher temperature is often in itself an advantage, and it is always an advantage, in industrial work, to be relieved from the necessity of using the strictest temperature control to avoid melting a furnace winding. This is especially true in cases where the time consumed in heating up the work in the furnace is important. For in these cases much time is saved by not using a constant current supply to the furnace winding but by first raising the current, upon the introduction of the cold work, and then bringing it down as the temperature of the work rises.

ELECTRICAL CONTACTS OF TUNGSTEN AND MOLYBDENUM.

Tungsten and molybdenum are destined to play a very important rôle in the field of contact-making devices. This is due to their high melting point, which prevents them from welding together; to their heat conductivity (about twice that of platinum) which tends to keep down local temperature rise; and to their hardness, which enables them to stand repeated impact without flattening out.

The natural assumption would be that both metals under the heat of even minute arcs, which form when the contacts are separated, would oxidize at the points where arcing has taken place and that non-conducting layers would thus be formed which would produce a high and variable contact resistance. But several things intervene to prevent this. First, there is the relatively good heat conductivity of the dense form of these metals, which distributes the heat. Then the fact that the metals are much less expensive than platinum, for example, makes possible the use of larger contact masses, which again militates against strong local heating. Finally, there is the fact that with both tungsten and molybdenum the oxides which form in the presence of a sufficiently limited amount of oxygen are conducting.

Some promising applications which are being tested out are the following:

As an iridium substitute in the "master" contacts of Tirrell voltage regulators.

As a silver substitute in the relay contacts of Tirrell voltage regulators.

As an iridium substitute in feed-wire voltage regulators.

As a platinum substitute in railway signal relays.

As a substitute for platinum-iridium in the contacts of a synchronously driven vibrating mechanical rectifier.

As a platinum substitute in telephone jacks.

As a platinum substitute in automobile and stationary gas-engine ignition work, for spark coil contacts, magneto circuit-breaker contacts, and spark plugs.

In connection with the above there was at first serious difficulty in getting satisfactory heat contact between tungsten or molybdenum on the one hand, and iron or brass, as the case might be, on the other.

This was due to the fact that neither tungsten nor molybdenum can be satisfactorily soldered by any of the ordinary processes. This difficulty has been finally entirely overcome.

TUNGSTEN AS TARGET IN A RÖNTGEN (X-RAY) TUBE.

This has proved to be, both from the scientific and practical points of view, an exceptionally interesting application.

Until recently platinum has been almost universally regarded as the best target material, and it has so long held undisputed sway in this field that the Röntgen ray worker has come to look upon its limitations as inherent in the Röntgen tube.

It has not been possible until recently to produce dense, forged pieces of pure malleable tungsten. But with the advent of this material, the possibilities of the Röntgen tube are greatly extended.

The desiderata in a material to be used as the anti-cathode or target are the following:

1. High specific gravity.
2. High melting point.
3. High heat conductivity.
4. Low vapor pressure at high temperature.

The reasons why the above qualities are desirable follow readily from a brief consideration of the theory of Röntgen-ray production.

From the concave cathode, electrically charged particles, the electrons, are shot out at high velocity in a direction normal to the surface. The paths of these particles converge and the target is placed at or near the point of strongest convergence, the focus point. When the electron meets an obstruction, as the target, its velocity is reduced, and the denser the target the more rapid is the deceleration. The more rapid the deceleration the greater is the amplitude of the electromagnetic pulse, the Röntgen-ray, sent out. Here then is a need for high specific gravity; that of forged tungsten is but little less than that of platinum.

In modern Röntgen-ray practice, powerful apparatus running sometimes to a capacity of six kilowatts is used to excite the tube. The greater part of the energy delivered to the tube is transformed into heat at the point where the cathode rays bombard the target. Where platinum is used it has been found necessary, to prevent melting, to place the target beyond the focus of the cathode so as to spread the bombardment over a larger area. As a radiograph is a shadow picture, and as the source of the Röntgen-ray is the bombarded area of the target, this enlarging of that area is clearly an undesirable thing to do, as the larger area will mean more overlapping and less definition in the resulting picture. In this way, the melting point of platinum has been the limiting feature of the Röntgen tube. The capacity of the tube has been increased by water cooling the platinum or by using as a target a large mass of copper having a very thin platinum face. But the limit, although raised by this artifice, has still been the melting point of the platinum.

Tungsten has a much higher melting point (3000° C. as against 1755° for platinum), and so, even with sharp focusing of the cathode rays on the target, permits the use of more energy than has hitherto been possible; for the high temperature to which it can run enables it to radiate more heat, and its better heat conductivity permits a more rapid flow of heat from the focus spot to the surrounding metal.

Stability of vacuum in a Röntgen tube is of the utmost importance, as the character of the rays is so largely determined by the vacuum. Metal, which under the influence of the high temperature vaporizes from the target, condenses on the glass in finely divided form and absorbs relatively large amounts of gas, thus changing the vacuum. At high temperatures tungsten vaporizes least of all the metals.

In the above case, practice seems to be in full accord with the theory, and the tungsten target offers great promise to the Röntgen-ray worker. It gives him what he has not had before, an indestructible target, so far as the present electrical apparatus goes, together with sharper definition and much shorter exposure.

TUNGSTEN PROJECTILES.

The use of wrought tungsten as a projectile is being carefully investigated. It offers, in this field, possibilities not possessed by any other metal.

The present small arm service projectile is made of lead with a jacket of copper-nickel alloy. The principal advantage of lead over iron, which would, of course be cheaper, is that it has a higher specific gravity. Because of this fact a lead bullet will have a smaller cross-section, and will therefore encounter less air resistance to its flight, than will an iron bullet of the same weight, and will therefore give a flatter trajectory and longer range. An iron bullet of the same diameter as the lead bullet could of course be given the same weight by increasing its length. But this would at once necessitate giving it a higher rotational velocity to keep its axis tangential to its flight. To impart this added rotational velocity calls for the expenditure of energy and so leaves less for velocity of translation. The lead bullet then with its higher density makes possible a flatter trajectory and longer range. With the exception of tungsten lead is the densest metal which can be considered for this purpose, for gold is the cheapest of the other elements having a higher specific gravity than lead. The density of wrought tungsten is 19.3 while that of lead is 11.5.

For military purposes, the softness of lead is not an advantage, a soft nosed bullet being tabooed in civilized warfare. For this reason and because of the fact that it is too weak to hold the rifling, it has to be jacketed with the copper-nickel alloy. To take the rifling and to act as a gas check, the tungsten bullet will require a copper band or its equivalent at the base.

The hardness and high tensile strength of wrought tungsten will give high penetrating power.

The high melting point of tungsten will prevent it from being harmfully upset at the base by the combined action of the high temperature and rapid impact due to the combustion of the powder charge.

(An unsymmetrical upsetting of the base of a projectile is very prejudicial to accuracy.)

It would be a very simple matter to calculate the constants of the trajectory of a tungsten projectile were it not for the fact that the high density removes it too far from the present base line. For such calculations one quantity is lacking, the so-called "form factor." This factor could itself be calculated if it contained, as the name would seem to imply, only the dimensions and the specific gravity; but there are also involved in it all of the errors due to simplifying assumptions which have been made in connection with the mathematical derivation of formulae. It therefore becomes necessary to experimentally determine the constants of the trajectory of tungsten bullets, and preparations for this work are now being made. W. D. COOLIDGE.

"THE FELLOW WHO DOESN'T KNOW ANY BETTER."

There are in the United States according to the census more than eight thousand chemists. Most of these chemists have spent at least three years and many have spent six or seven years in the college or university acquiring a knowledge of chemistry. Above all other men they are acquainted with chemical laws and processes. According to President Maclaurin and President Lowell, to judge from some of their comparatively recent addresses, the earth and the fulness thereof during the present century is to belong to the chemist. Aside from his meekness, however, does the chemist today show any indications of entering into his inheritance? Is the chemist today, in this country, originating as many new products and processes as he should? Is he even originating his fair proportion of new chemical products and processes?

In the older and more strictly chemical industries, such as the acid, heavy chemical, alkali and dyestuff industries for instance, the chemist seems to be in control and progress in these industries may be credited to him. But there are other industries in which chemical principles of the highest order are involved which for the most part are not under chemical control; such as, the paint, varnish, dyeing, leather, alloy, shoe ink and shoe polish industries. There are in some instances chemists in control who are making good, but for the most part the chemist in such industries as are mentioned above is employed in testing raw materials and finished products. He may be even essentially ignorant of the manufacturing processes.

Consider, for example the manufacture of shoe inks and polishes. These are important industries and the manufacture of these products is a chemical process. Moreover, American shoe inks and polishes are sold all over the world, some of our largest companies having branch factories in England, Germany and France. But in this essentially chemical industry there are almost no chemists. Their products and processes have, for the most part at any rate, originated with rule-of-thumb men, the so-called practical men. Conditions in the other industries mentioned are similar, though in a lesser degree perhaps.

The first really successful one-set edge ink for shoes was stumbled on by a man who added a basic color to an emulsion of carnauba wax and soap, instead of an acid color as called for by the formula. If he had been a chemist he would have known better. He would have known that a basic color would undergo double decomposition with the soap, causing a coagulation of the emulsion. That is just what the basic color did in this case, but after stirring and straining it was just as fluid as before. The blacking man now throws his wax with acid to get the desired result. What chemist in his right mind would have added acid to an emulsion of wax and soap expecting to obtain a desirable result?

It keeps the chemist busy stretching his conception of chemical laws, theories and hypotheses to explain how the despised rule-of-thumb man gets the results he does.

The chemist, at any rate the common, garden-variety of chemist, suffers from a sort of *chemico-sclerosis*. His conceptions of chemical laws become hardened and his theories and hypotheses inflexible. He knows that sodium chloride added to a silver salt solution produces a precipitate, but until colloids became fashionable how many chemists knew that in the presence of a protective colloid-like albumen the silver chloride would not precipitate? He knows that silver iodide, bromide and chloride are insoluble and concludes that silver fluoride is also. He knows that hydrogen sulphide gives black mercuric sulphide with a solution of mercuric chloride and so the United States Pharmacopoeia states that under the conditions of the 'Gutzeit Test' for arsenic, hydrogen sulphide gives a black stain. Under usual conditions, however, the stain is yellow and may be thought to indicate arsenic.

The chemist finds it difficult to work without a theory and neglects to follow the leads that according to his theory do not promise results. But results have been obtained that were not in exact accordance with the preconceived theory. Perkin had a theory for making quinine and found the first aniline dye in spite of this theory.

There is also a certain chemical snobbery that prevents chemists following leads of dubious respectability. In 1873 it was discovered that a dye resulted from the fusion of sawdust and sodium sulphide. The dye was weak and of no ascertainable constitution, but that such a fusion gave a dye at all was a highly significant fact and even a moderate amount of investigation would have improved this dye tenfold. But as the father of the dye was sawdust, of course, no self-respecting chemist would recognize it, and nothing was done on sulphur colors until twenty years later a sulphur dye of perfectly respectable parentage was discovered. Then hundreds of chemists were set to tilling the field.

The practical, rule-of-thumb man with a natural bent for research labors under none of these handicaps. He is free. He staves ahead untrammeled by theory and now and then gets the result. He

may put on the market a wood stain reeking with ammonia as an *acid* stain but it sells and does the work. He gets results often enough to lend a color of truth to the statement that "It's generally the fellow who doesn't know any better who does the thing that can't be done.

The fellow who doesn't know any better," will not make this century the century of chemistry. It will be done by the chemist who realizes the flexibility of our great laws, the instability of hypothesis, the unreliability of analogy and who is not afraid of the dark. W. H. WATKINS.

ORIGINAL PAPERS.

DETERIORATION AND SPONTANEOUS HEATING OF COAL IN STORAGE.[1]

By HORACE C PORTER AND F. K. OVITZ.

Received December 11, 1911.

Not many years ago, coal was commonly regarded as an extremely unstable material, subject to very serious alteration and losses on exposure to the elements. E. C. Pechin, in 1872, speaking before the American Institute of Mining Engineers, says: "Fuel suffers materially by storage; especially with bituminous and semi-bituminous coals is the loss heavy, an exposure of only two weeks causing a loss of carbon to the extent of 10 to 25%." Similar views have been held in much more recent times. For example, in a paper before the U. S. Naval Institute in 1906 we find the statement: "The pressure of the weight of coal causes gases to be evolved; these gases constitute the chief and only value of the coal in that they furnish the heat units. It is claimed that if a ton of fine bituminous coal be spread out on a concrete pavement in the open air in this climate (Key West, Florida) for one year, it will lose all its calorific properties. The gases are simply free to escape, and when the coal has lost all its gas it will have lost all its heat units and be simply coke." This was only five years ago.

In 1907 a German gas-works engineer claims to have found that moist fine coal sustained an average loss per week of 1.7 per cent., this loss being due to gas. The 1889 edition of Groves and Thorp's "Chemical Technology of Fuels" says: "In some places coal is known to lose 50 per cent. of its heating value in six months." Other statements like these are to be found in recent literature, but probably the great majority of chemists and engineers to-day hold no such exaggerated ideas on the subject. There is, on the other hand, a well-defined suspicion, in the minds of many that sufficient loss of volatile matter and sufficient deterioration by oxidation does occur in coal to be of industrial importance; and for that reason the investigations described in this paper were undertaken by the Bureau of Mines to determine accurately the extent of the deterioration in different types of coal.

First a study was made in the laboratory of the loss of volatile matter from crushed coal during storage. A number of samples (20 lbs. each), representing a variety of types from widely separated fields, were broken to about $^1/_2$-inch size and immediately placed in glass bottles in the mine. At the laboratory the accumulated gas was withdrawn and a free continuous escape of the volatile products permitted at atmospheric pressure and temperature. The results of these experiments have been published in Technical Paper No. 2, Bureau of Mines, entitled "The Escape of Gas from Coal" and will therefore not be given here in detail. Suffice it to say that while several coals evolve methane in large volumes especially in the early period after mining the coal suffered in one year a loss in calorific value from this cause of but 0.16 per cent., as a maximum.

It seems therefore that the loss due to escape of volatile matter from coal has been greatly overestimated.

At the instance of the Navy Department, however, which is a purchaser of coal to the extent of two or three million dollars annually, and stores large lots in warm climates for long periods of time, more elaborate tests were undertaken to determine the total loss possible in high-grade coal by weathering. The extent of the saving to be accomplished by water submergence as compared to open-air storage was a point to be settled, and there had also arisen the question as to whether salt water possessed any peculiar advantage over fresh water for this purpose. An English railway and dock superintendent in an article in the London *Engineer*, 1903, reports that he has found coal accidentally submerged for 10 years in the salt mud of the English Channel, actually improved in calorific value by 1.8 per cent. which offers a very pretty question to chemists to say why." He claims that salt will preserve the virtues of coal as it does those of many other things, "if coal is given a strong dose of coarse salt and water 12 hours before using, its calorific value is greatly improved."

Coal-storage problems have assumed importance during the last few years on account of the uncertainties of supply due to strikes and transportation difficulties. The naval coaling stations, the Panama R. R. Co., the Great Lakes commercial coal distributing companies, large coke and gas or power plants at a distance from the coal fields and the railroads themselves, particularly those in the west, keep 50,000–500,000 tons in storage a great deal of the time.

In brief outline, the tests by the Bureau were carried out as follows: four kinds of coal were chosen: New River on account of its large use by the Navy; Pocahontas as a widely used steaming and coking

[1] Presented, by permission of the Director, Bureau of Mines, at a joint meeting of the New York Section, American Chemical Society, American Electrochemical Society, and the Society of Chemical Industry, New York, November 10, 1911.

coal in the eastern section, and as being also the principal fuel used in the Panama canal work; Pittsburgh coal as a type of rich coking and gas coal; and Sheridan, Wyoming, subbituminous or "black lignite"—a type much used in the west. With the New River coal, 50-pound portions were made up out of one large lot, which had been crushed to $^1/_2$-inch size and well mixed. These portions confined in perforated wooden boxes were submerged under sea water at three navy yards, differing widely from each other in climatic conditions, and 300-pound portions from the same original lot were exposed to the open air, both out of doors and indoors, at the same places.

With the Pocahontas coal test was made only at one point, the Isthmus of Panama—run-of-mine coal being placed in a 120-ton pile, exposed to the weather. Pittsburgh coal was stored as run-of-mine in open outdoor bins, 5 tons capacity, at Ann Arbor, Michigan, also in 300-pound barrels submerged under fresh water. The Wyoming subbituminous was stored at Sheridan, both as run-of-mine and slack in outdoor bins, holding three to six tons each.

Every test portion was sampled each time in duplicate and in all cases except the outdoor pile at Panama and the 300-pound open-air piles of New River coal the sampling was done by rehandling the entire amount. In the excepted cases mentioned it was not thought fair to disturb the entire lot, and therefore at Panama a vertical section of ten tons only was removed each time (eight samples being taken from the 10-ton section), while in the case of the outdoor lots at the Navy Yards a number of small portions, well-distributed, were taken from each pile, mixed, and quartered down.

Small lots and a fine state of division were conditions purposely adopted with the New River coal so as to make the tests of maximum severity.

Moisture, ash, sulphur, and calorific value determinations were made on each sample, the latter by means of the Mahler bomb calorimeter and a carefully calibrated Beckmann thermometer. The calorimetric work on all except the Sheridan, Wyoming, tests has been done throughout by one man, Mr. Ovitz, and with the same instrument. All the calorific values in the tables have been calculated to a comparable unit basis, viz., that of the actual coal substance free of moisture, sulphur, and corrected ash.

The results show in the case of the New River coal less than 1 per cent. loss of calorific value in one year by weathering in the open. There was practically no loss at all in the submerged samples and fresh water seemed to "preserve the virtues" of the coal as well as salt. There was almost no slacking of lump in the run-of-mine samples and the crushed coal in all cases deteriorated more rapidly than run-of-mine.

The Pocahontas run-of-mine in a 120-ton pile on the Isthmus of Panama lost during one year's outdoor weathering less than 0.4 per cent. in heating value, and suffered little or no physical deterioration of lumps.

The Pittsburgh gas coal during six months' outdoor exposure suffered no loss whatever of calorific value, measurable by the calorimetric method used, not even in the upper surface layer of the bins.

The Wyoming coal lost as much as 5.3 per cent in one of the bins during two and three quarter years, and 3.5 per cent. even in the first three months. There was bad slacking and crumbling of the lumps on the surface of the piles but where the surface was fully exposed to the weather this slacking did not penetrate more than 12–18 inches in the $2^3/_4$-year period.

No outdoor weathering tests have been made by the Bureau on coal of the Illinois type. Thorough tests, however, on this type have been reported by Prof. S. W. Parr, of the University of Illinois, and by A. Bement, of Chicago, both of whom find from 1.0–3.0 per cent. in calorific loss in a year by weathering. Mr. Bennet reports a slacking of lumps (in tests on small samples) of over 80 per cent. in one case and about 12 per cent. in another. It is probable that in this type as in the Wyoming, the slacking in a large pile would not penetrate far from the surface.

Storage under water unquestionably preserves the heating value and the physical strength of coal. But it practically necessitates firing wet coal, and therefore means the evaporating in the furnace of an amount of moisture varying from 1–15 per cent., according to the kind of coal. This factor is an important drawback to under-water storage with coals like the Illinois and Wyoming types, which mechanically retain 5–15 per cent. of water after draining, but in case of the high-grade eastern coals, if firemen are permitted, as is ordinarily the case, to wet down their coal before firing, "so as to make," as they say, "a hotter fire," then the addition during storage of the 2 or 3 per cent. moisture which these coals retain would be of little consequence. Submergence storage is an absolute preventative of spontaneous combustion, and on that account alone its use may be justified with some coals, but merely for the sake of the saving to be secured by avoidance of weathering there does not seem to be good ground for its use.

SPONTANEOUS COMBUSTION.

Losses in coal due to spontaneous heating are a much more serious matter. Oxidation, *i. e.*, probably in the main an absorption of oxygen by the unsaturated chemical compounds in the coal substance, begins at ordinary temperature in any coal, attacking the surfaces of the particles, thus slowly developing heat. In a small mass of coal this slowly developed heat can readily dissipate itself by radiation and no rise in temperature results. If radiation is restricted, however, as in a large pile densely packed, the temperature slowly rises. Now, the curve of oxidation rate plotted against temperature rises with great rapidity, and when the storage conditions are such as to allow a certain point (near 100° C.) to be passed the rate of oxidation is great enough ordinarily so

that the heat developed overbalances the heat radiated and the temperature will rise to the ignition point if the air supply is adequate. The importance therefore can be seen of guarding against even moderate heating in the coal either from internal spontaneous causes or by radiation from external sources. Increased loss of heating value and of volatile matter occurs at moderately increased temperatures even though the ignition point is not reached.

The amount of surface exposed to oxidation in a given mass depends on the size of the particles and increases very rapidly as the fineness approaches that of dust. Dust is therefore a dangerous thing in a coal pile, particularly if it is mixed with larger sized coal which forms air passages to the interior. Spontaneous combustion is brought about by slow oxidation in an air supply sufficient to support the oxidation but insufficient to carry away all the heat formed. There is a wide variation among coals in friability. In comparative rattler tests under certain standard conditions, Pocahontas, New River and Cambria Co., Pa., coals produced nearly twice as much dust (through $^1/_8$" screen) as a sample from the Pittsburgh seam. This is a large factor in spontaneous combustion. Mixed lump and fine, *i. e.*, run-of-mine, with a large percentage of dust, and piled so as to admit to the interior a limited supply of air, make ideal conditions for spontaneous heating.

High volatile matter does not of itself increase the liability to spontaneous heating. A recent circular letter of inquiry on spontaneous combustion sent by the Bureau to more than 2,000 large coal consumers of the United States has brought 1,200 replies, of which 260 report instances of spontaneous combustion, 220 of them naming the coal. Of these 220, 95 are in semi-bituminous low-volatile coals of the Appalachian region, and 55 in western and middle western coals. This result shows at least no falling behind on the part of the "smokeless" type and no cause for placing special confidence in these coals for safety in storage.

A serious fire in cinder filling under a manufacturing plant in Pittsburgh was recently investigated by the Bureau and all the evidence pointed to spontaneous combustion as the cause, induced by external heat radiated from a furnace. The cinders contained 40 per cent. of carbon. A similar fire occurred two years ago in cinder filling under a smelting plant on Staten Island in which case the cinders contained 33 per cent. carbon. Damage amounting to $20,000 was done. The cause was not definitely determined, but from the reports of the insurance adjusters spontaneous heating appears to be the most plausible explanation The volatile matter in the material could not have been a factor in these causes.

Pocahontas coal gives a great deal of trouble with spontaneous fires in the large storage piles at Panama. It is reported also by several large by-product coke concerns to be more troublesome in this respect than their high volatile gas coals. The high volatile coals of the west are, to be sure, usually very liable to spontaneous heating, but they owe this property to chemical nature of the substances which compose the coal rather than to the amount of volatile matter. Strange as it may seem, a high oxygen content in coal appears to parallel its avidity for oxygen and to promote therefore its tendency to spontaneous combustion.

The influence of moisture and that of sulphur upon spontaneous heating of coal are mooted questions much discussed, not very much actually investigated, and certainly not yet settled. *Richters* has shown that in the laboratory dry coal oxidizes more rapidly than moist, but the weight of opinion among practical users of coal is that moisture promotes spontaneous heating. The observation by the Bureau of many actual cases has not developed any instances where moisture could be proven to have had such an effect. Sulphur on the other hand has been shown by these investigations, to have in most cases only a minor influence. In a number of actual cases, samples of the heated coal from areas where the heat was greatest have been analyzed, both for the total sulphur and that in the sulphate form. The difference between these, or in other words, the unoxidized sulphur was in no case less than 75 per cent. of the average total sulphur in the original. In other words, not more than $^1/_4$ of the total sulphur has entered into any heat-producing reaction. The possibility remains, however, that all of the sulphur which was oxidized was concentrated in one pocket of moist flaky pyrites, and thus sufficient heat was developed in one spot to act as an igniter. On the other hand, a Boston company, using Dominion (Nova Scotia) coal of 3–4 per cent. sulphur, has much trouble with spontaneous fires in storage, but a number of samples taken by the Bureau from exposed piles of this coal in which heating had occurred showed that 90 per cent. of the sulphur was still unoxidized. Experiments in the laboratory, passing air over coal at 120° C., have developed enough heat to ignite the coal and no change was found in the form of the sulphur. While not entirely conclusive, these results point to a very minor contribution, if any, on the part of sulphur to spontaneous heating in coal.

Freshly mined coal and even fresh surfaces exposed by crushing lump coal exhibit a remarkable avidity for oxygen, but after a time become coated with oxidized material, "seasoned" as it were, so that the action of the air becomes much less vigorous. It is found in practice that if coal, which has been stored for six weeks or two months and has even become already somewhat heated, be rehandled and thoroughly cooled by the air, spontaneous heating rarely begins again. A large power plant in New York crushes its coal to pass a 4" screen immediately after unloading from barges, the fines and dust, 50 per cent. or more, being left in the coal to be stored. This freshly crushed coal is elevated to iron hopper-shaped bunkers directly over the boilers and the air temperature in these often reaches 100° F. As the coal hangs on the sloping sides sometimes three or four months at a time, it seems hardly surprising that some of the bunkers are on fire practically all of the time.

With full appreciation of the fact that any or all of the following recommendations may under certain conditions be found impracticable, they are offered as being advisable precautions for safety in storing coal whenever their use does not involve an unreasonable expense:

(1) Do not pile over 12 feet deep nor so that any point in the interior will be over 10 feet from an air-cooled surface.

(2) If possible, store only lump.

(3) Keep dust out as much as possible; therefore reduce handling to a minimum.

(4) Pile so that lump and fine are distributed as evenly as possible; not as is often done, allowing lumps to roll down from a peak and form air passages at the bottom.

(5) Rehandle and screen after two months.

(6) Keep away external sources of heat even though moderate in degree.

(7) Allow six weeks' "seasoning" after mining before storing.

(8) Avoid alternate wetting and drying.

(9) Avoid admission of air to interior of pile through interstices around foreign objects such as timbers or irregular brick work; also through porous bottoms such as coarse cinders.

(10) Do not try to ventilate by pipes as more harm is often done than good.

THE DISTILLATION OF ALCOHOL.[1]

By A. B. Adams, Chief Chemist, Internal Revenue Bureau.

Received July 13, 1911.

The production of alcohol differs essentially from the production of straight whiskey, because it is necessary that the finished product be as near pure ethyl alcohol as is possible, by mechanical means, to distil. To effect this the processes are essentially the same up to a given point; that is, as far as the primary distillation, this being conducted in a continuous beer still which is built exactly similar to the continuous beer still used in a majority of the "Bourbon" houses. The distillate, however, is produced at a much higher proof, generally at about 160 degrees or 80 per cent. alcohol by volume. The high wine distillate is reduced with water to about 101 proof, and passed through charcoal filters under pressure. After filtering, the spirit is emptied into the kettle of the "column" still. This still consists of a series of plates ranging in number from 18 to 30 or more, depending on the type and size of the plant. These plates act as dephlegmators, each one constantly condensing the products of higher boiling points, permitting the products of lower boiling points to proceed upward. When the vapors leave the top of the still they enter a series of condensers, in some types, called a "goose," which consists of a series of pipes arranged very much like a radiator. These pipes are surrounded by cooling water at a temperature practically one degree higher than the boiling point of ethyl alcohol. The purpose of this apparatus is to condense all products as far as possible, which boil at a higher temperature than ethyl alcohol and which have escaped the action of the plates in the still. From the "goose" the vapors pass into the condenser. In recent years, on account of the excessive weight of the "goose," which in some distilleries is a tank as large as a good-sized room, a simpler apparatus has been devised, called a "tubular separator;" this operates on the same principle as the "goose," namely, is cooled by water at the same temperature. This is considered by many to be as efficient a piece of apparatus.

At the "tail box" or end of the condenser, the distillate is separated into various fractions, depending on the quality, by the operator of the still. These are generally called, in the order distilled, "foreshots," or low wines, "heads," "middle run," "tails," "low wines" and lastly, "fusel oil." The point at which the different fractions are cut out depends upon the class of goods desired by the operator. The "middle run" is the cleanest part of the distillation, and when a very clean spirit is desired is frequently separated in a No. 1 and a No. 2 spirit. The "foreshots" and low wines are the poorest parts of the run, containing the greatest amount of bad smelling impurities, which render them unfit for commercial purposes. In this condition they are generally collected for several days and then redistilled in the "column." (The better part of such a redistillation is classed as "commercial alcohol.") The "heads and tails," if separated fairly clean, are combined and called "commercial alcohol." The "middle run," No. 1 and No. 2 spirit go into the trade as such. The "fusel oil" is not run off at the end of each charge but is permitted to remain in the still and on the plates of the column until two or more charges have been run, when, in the judgment of the distiller, sufficient "fusel oil" has been collected to warrant its distillation; this is conducted by simply turning on more steam when the last of the "low wines" have been run from the charge then in the kettle.

The last portion of the "low wines" will consist of increasing proportions of fusel oil and water. When the per cent. of fusel oil is so great that it does not remain in solution, the flow in the tail box becomes milky, and the subsequent distillate is distilled into the "fusel oil" tank. The fusel oil is gradually forced up the column from plate to plate, being carried upward by "steam distillation." Although water is of a lower boiling point than the amyl alcohols, yet it does remain on the plates of the column after the fusel oil has been driven up. This can be proven by opening the try cocks at each plate in the still during the course of the distillation.

METHODS OF ANALYSIS.

The analytical methods used were those as found in *Bulletin* **107**, Bureau of Chemistry, Department of Agriculture, under "Distilled Liquors," with changes in treatment for esters and higher alcohols.

Proof.—The proof of the samples was determined

[1] Published by authority of the Commissioner of Internal Revenue. See companion article, "The Distillation of Whiskey," This Journal, Feb., 1910.

with a regular Internal Revenue hydrometer. One degree of proof is equal to one-half of one per cent of alcohol by volume.

Acids.—Fifty cc. titrated with $N/10$ NaOH; use phenolphthalein as indicator; calculated to acetic acid.

Esters.—Saponify with soda, titrate excess with sulphuric acid, calculate results to ethyl acetate. The above method was used for the determination of esters in all of the samples but the following: Nos. 36814 to 36826, inclusive; in these samples, on account of the content of aldehyde bodies, the true ester value could not be determined until they were removed. These samples were treated by the method as given in *Allen*, Third Edition, page 158. The spirit being treated with 1 cc. aniline and 1 cc. phosphoric acid, refluxed, distilled, then proceed in regular manner. I find that this method gives results a trifle lower than are correct, but this was compensated for by adding a correction.

Higher Alcohols.—The Allen-Marquardt method was used. Samples Nos. 36814 to 36828 had to be treated to remove the aldehydes and acetals. This was done by successive treatments with alkali to form condensation products, distilling; then treat with HCl to break up the acetal into aldehyde; then treat with alkali and distil, repeating until the distillate was clean. Blanks were run to see that this treatment would give true results.

Aldehydes.—Determined according to the prescribed method, being a colorimetric comparison. Test made with a solution of fuchsin dissolved in SO_2.

Furfurols.—Used prescribed method, a colorimetric comparison. Test made by treating the spirit with 2 cc. aniline and $^1/_2$ cc. hydrochloric acid.

In proceeding with the plan of the work outlined a distillery was selected which produced alcohol as a by-product from the manufacture of yeast. The mash is made in the usual manner in about the following proportions: Malt 34%, rye 5%, corn 61%.

Fermentation.—The fermentation is a very rapid one as the mash is aerated during the entire process, which is complete in sixteen hours. The result of such aeration produces a very pure and a very strong yeast, but at the expense of more or less alcohol which is lost by evaporation, and more particularly by oxidation into aldehydes, etc. On account of the high aldehyde content in such a mash or "beer" it is acknowledged to be one of the most difficult to distil clean; that is, to obtain a good grade of alcohol .

Primary Distillation.—The finished fermentation, or as it is called, the "beer," is distilled in a large continuous beer still, the operation of which is described in a previous article.[1]

The still is three feet in diameter, containing fourteen chambers, each eighteen inches in height. It produces continuously a spirit of about 150 proof, called "high wines." Such a still after it has been once set produces a similar distillate during its entire period of operation, except at the beginning and end, when a full head of beer is not on the still.

Filtration.—The product of the beer still is reduced to about 101 proof with pure water and is then passed through charcoal filters under pressure. These filters are cast iron receptacles about $3^1/_2$ feet high by 4 feet in diameter, tightly packed with charcoal. The purpose of such filtration is to eliminate from the high "wines" some of the raw odors of the spirit. It was at one time thought that this filtration, or as it is erroneously called, rectification, removed the fusel oil. The results of the analysis of these samples, as well as of the products of six other distilleries using similar filters, prove this to be incorrect, as the analyses in no case show more than a slightly lower per cent. of higher alcohols.

For example:

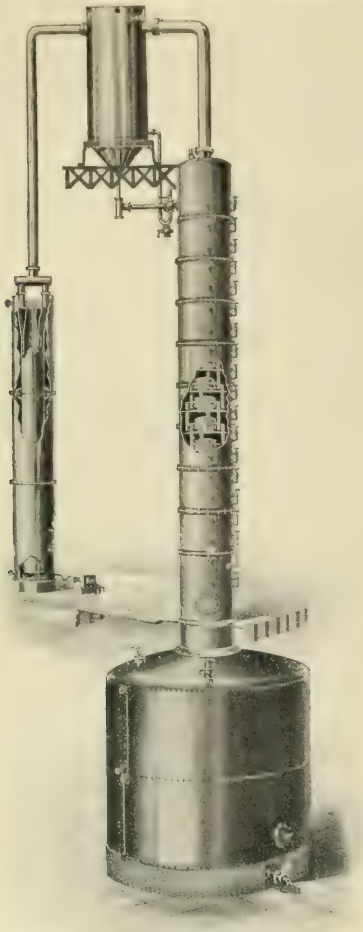
	Higher alcohols. Grams per 100 liters.
Sample No. 36,814: Distillate from beer still after reduction.....	100.2
Sample No. 36,815: Distillate from beer still after reduction.....	84.2
Sample No. 36,816: Average sample of the above after having been through the charcoal filters.....	86.2

In my opinion this filtration removes from the spirit the major portion of certain bodies which are formed during fermentation and which are soluble in water and not in the spirit, probably decomposition products from the proteids of the grain.

Redistillation.—The construction of the column still can best be understood by referring to the illustration and the cross section of two of the plates. Four thousand gallons of high wines, which had been reduced to 101° proof and filtered through charcoal, were placed in the kettle; it is heated by means of a closed steam coil. The vapors pass up from the kettle, entering the still at the bottom, as they ascend, striking the bottom of the first plate. A portion of the vapors is condensed; the larger portion proceeds upward through the three pipes which are underneath the "bonnets." As the water level of each plate reaches exactly to the height of the down pipe, the vapors, as they leave the bonnet, have to pass through this level of liquid. More of the vapors are condensed, the remainder pass upward against the next plate and enter the bonnets, and so on. Those products which are condensed flow downward, a constant level being kept on the plates by means of the down pipes. Products which flow to the bottom of the still are returned to the kettle automatically. The column still from which the samples were taken has twenty-three chambers and one boiling dome. The vapors after passing through the highest chamber enter a tubular separator, as previously explained; this is kept very near the boiling temperature of ethyl alcohol. Any products which are condensed are returned to the top of the still by means of the small trapped pipe. The vapors on leaving the separator enter the condenser where they are condensed to a liquid. It takes about thirty hours to run off one charge of the kettle. Three charges of the kettle are run and the fusel oil distilled on the third running

[1] THIS JOURNAL, Feb., 1910.

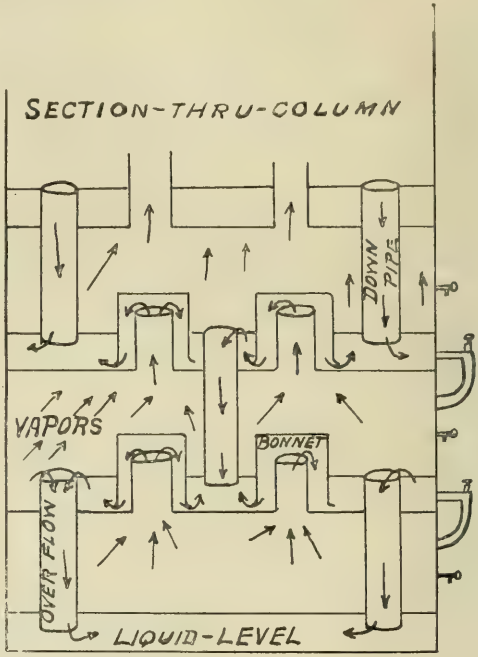
only, the still being thoroughly cleaned out after this distillation. The samples were taken from the running of such a third charge, and, therefore, include fusel oil samples. By referring to the analytical table

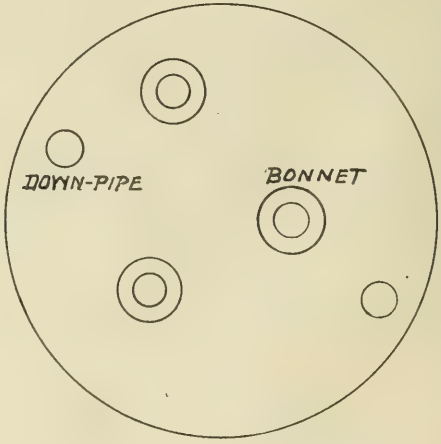


it will be seen, when the samples were taken, what part of the run they represent, and the analysis. Only three samples were taken during the middle run because necessarily this would be a clean spirit. More frequently samples were taken at the beginning of the distillation and at the end on account of the changes occurring in these portions of the runs.

The first two samples, Nos. 36817 and 36818, are not representative of the very first runnings of the charge in the kettle at the time, but contain an admixture of products left on the plates from the two previous distillations. When the third sample, No. 36819, was taken, the still appeared to be running on the charge in the kettle; this is shown by the drop in the proof. The proof gradually rises until 191° is reached which is the highest proof wanted. The speed of the distillation is regulated by the operator, it being desired to eliminate, in the first part of the distillation, as much as possible of the aldehydes and similar products. After the middle run has been distilled the proof gradually drops. It could not be read after 12.21 P.M., when it was 165°. It goes lower than this but as the flow of spirit in the tail box is cut out of the hydrometer cup in order not to foul it with fusel oil, the reading could not be made.

Acids.—There is a constant appearance of acids in the distillate, although the highest percentage appears in the first portions of the run. By the time the middle run is reached the spirit is nearly free of this constituent.





Esters.—The same thing can be said of esters as of the acids.

The Higher Alcohols.—The results of the first three samples show a rather definite percentage of

higher alcohols. I am of the opinion that this is due, not so much to the distillation of this charge, but to the fact that fusel oil which had remained upon the plates from the previous distillation, had been forced up the still and into the tail box before the still could be regulated. In the next sample the content has dropped to 19 which is a rather small amount. These results practically remain constant throughout the remainder of the distillation, until about the tail is reached, when the percentage of higher alcohols begins to increase. It is very noticeable in sample No. 36835. In the sample taken forty-five minutes later it has increased to nearly a per cent. In the sample taken sixteen minutes later it has increased to 2.6 per cent., and in the last sample taken, which was just before the "fusel" began to distil, the content was over 16.3 per cent.

Aldehydes.—As previously stated, alcohol produced by the aeration of the mash contains an excessive amount of aldehydes. A large portion of the aldehydes go over in the first runnings, the majority having been driven off at the end of two hours' distillation. When the middle run is reached the content of aldehyde is almost *nil* and remains so throughout the distillation, showing that practically all the aldehydes have been distilled.

Furfurol.—No furfurol was found in the products of the beer still, and none was found in the distillate of the column. These results bear out the statement, previously made from this laboratory, that furfurol had never been found in the distillate from a continuous beer still.

Acetal.—The percentage of acetal and similar bodies, other than aldehydes, was not determined, there being no feasible method. The presence of acetal is shown in samples 36814 to 36828, inclusive; only a very small amount was found in the last few samples. It is to be expected that such bodies will be present in spirit when such a high percentage of aldehydes is contained therein, these products being produced by the action of the aldehydes on ethyl alcohol.

Quantities in Each Fraction.—Of the 4,000 gallons of 101 degrees proof of spirit in the charge of the kettle, neglecting the water, about 3 per cent. is separated as "fore-shots" (low wines), 30 per cent. as "heads," 48 per cent. as "middle run," 16 per cent. as "tails" and 3 per cent. as low wines, fusel oil, 0.25 per cent. An examination of the samples both physical and chemical would indicate that the fractions represented by the two samples taken before, and the two samples taken after the middle run could, without detriment, be added to the higher grade spirit increasing the proportion of "middle run" to about 63 per cent. In a distillery producing alcohol from an unaerated mash the proportion of "middle run" is as would be expected larger than this figure, being between 65 and 80 per cent., depending entirely on the quality desired.

SAMPLES FROM THE PLATES OR CHAMBERS.

In order to see at just what stage the purification of the alcohol occurs, it was decided to take samples from the plates of the still from the bottom up. The analyses of these would show at just which point the spirit was cleansed. As previously stated, the charge in the kettle, which was sampled, was a third one; there was, therefore, remaining on the plates and in the kettle just three times as much higher alcohol as was present in one charge. I thought it best to wait until the still has been cleaned out and a new charge in process of distillation before taking samples from the plates. The best time at which to take representative samples is during the middle of the distillation, when the purest spirits come over. I, accordingly, went to the distillery at 10 o'clock P.M., at which time the middle run had been distilling for two hours. By referring to the illustration it will be seen that there is a little cock just above each plate in the still. The cocks are placed about four inches above the water line of the plate. Being so high it made it difficult to obtain samples in some cases, as only vapor came from the cock. The three chambers nearest the bottom could not be sampled as the cocks had been permanently closed. Samples were taken from Nos. 4, 5, 6 and 7 chambers from the bottom, and then from every other chamber to the top, or 23*d* making twelve samples. For purposes of comparison I have included in this table Sample No. 36829 which is a sample from the previous run, taken at the condenser, at about the same relative time, showing that the highest proof is reached in the top chamber of the still. By reference to the analytical table and curves it is seen that the proof rather regularly increases from the fourth chamber, where it was 164°, to the top chamber where it was 190.7°.

Acids and Esters.—The content of the acids and the esters would seem to indicate that both of these products are formed in the column, as, if this were not the case, there would be no reason for a higher content in the upper than in the lower chambers.

Higher Alcohols.—Examination of the higher alcohols proves that the major portion of them is condensed out of the spirit on the lower plates, and when the seventeenth chamber is reached it is as free of this product as the still can make it.

Aldehydes.—The determination of aldehydes show only a faint trace.

Furfurol.—No furfurol was found in any of the samples.

CONCLUSIONS.

The results seem to prove that the essential differences between the column still and the pot still, or what should probably be called a "simple" still, are:

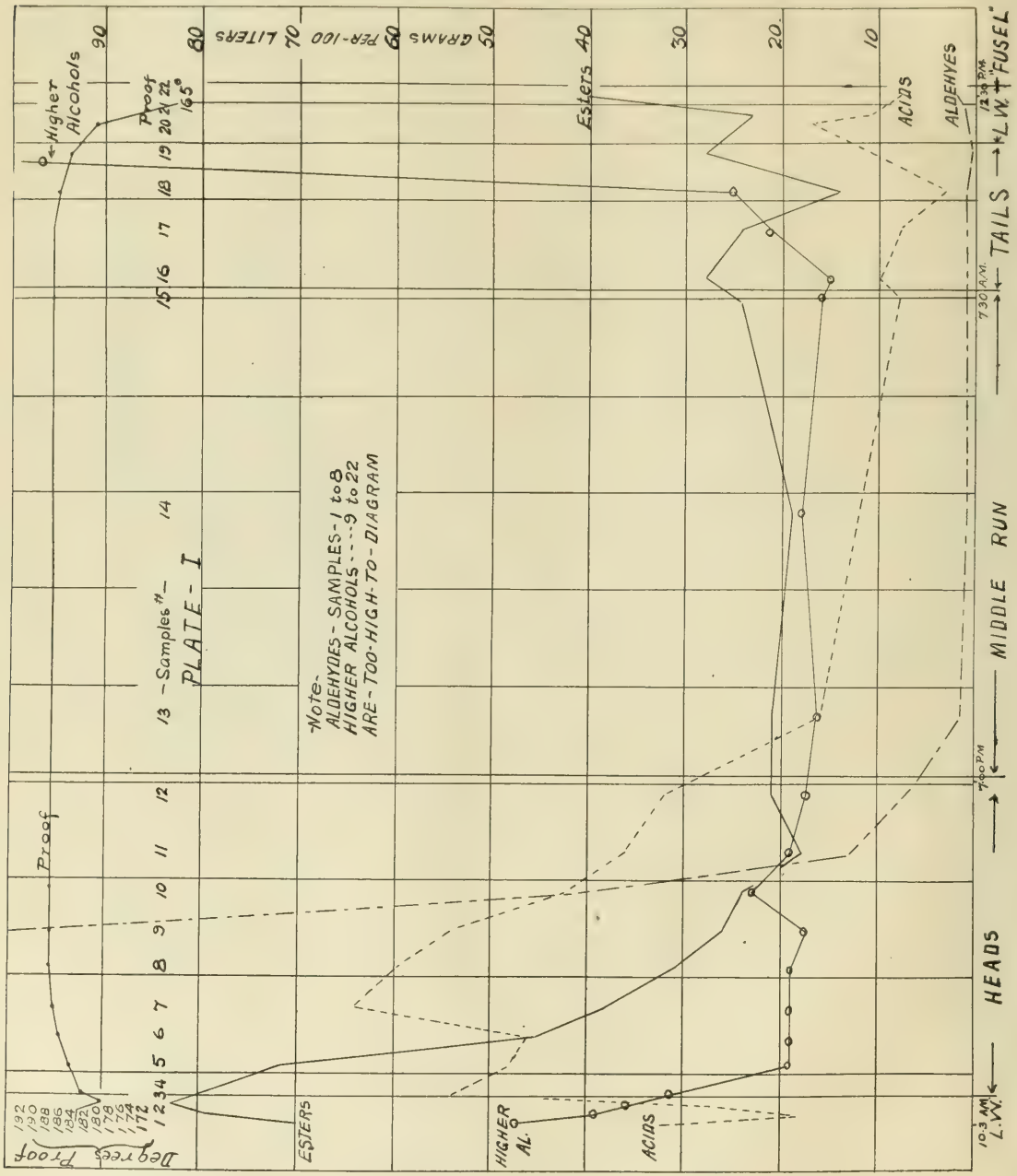
First: That a much higher proof can be obtained from the former.

Second: That the system of chambers, the source of heating being a steam scroll, fractionates, from the middle portion of the run, practically all of the higher alcohols, namely, about 80 per cent., whereas the simple still not only does not fractionate any of these constituents, but the greatest portion distils over in the middle part of the run.

Credit should be given Mr. Peter Valaer for the analytical work on the aldehydes and furfurols.

I wish to thank The American Copper & Brass Works, of Cincinnati, Ohio, for the loan of the cut of the column still.

NOTE.—In offering this paper I would state that it is not as complete as it might be, as more work should be done to ascertain the different constituents of the foreshots and heads, and also the relative proportions of the different higher alcohols in the last portion of the run. For instance, sample No. 36838 gives, with the Allen-Marquardt method, for higher alcohols, 16.3 per cent. by weight; this would be approximately 20 per cent. by volume. After shaking this sample with a large volume of water 40 per cent. of higher alcohols separate, of which a considerable



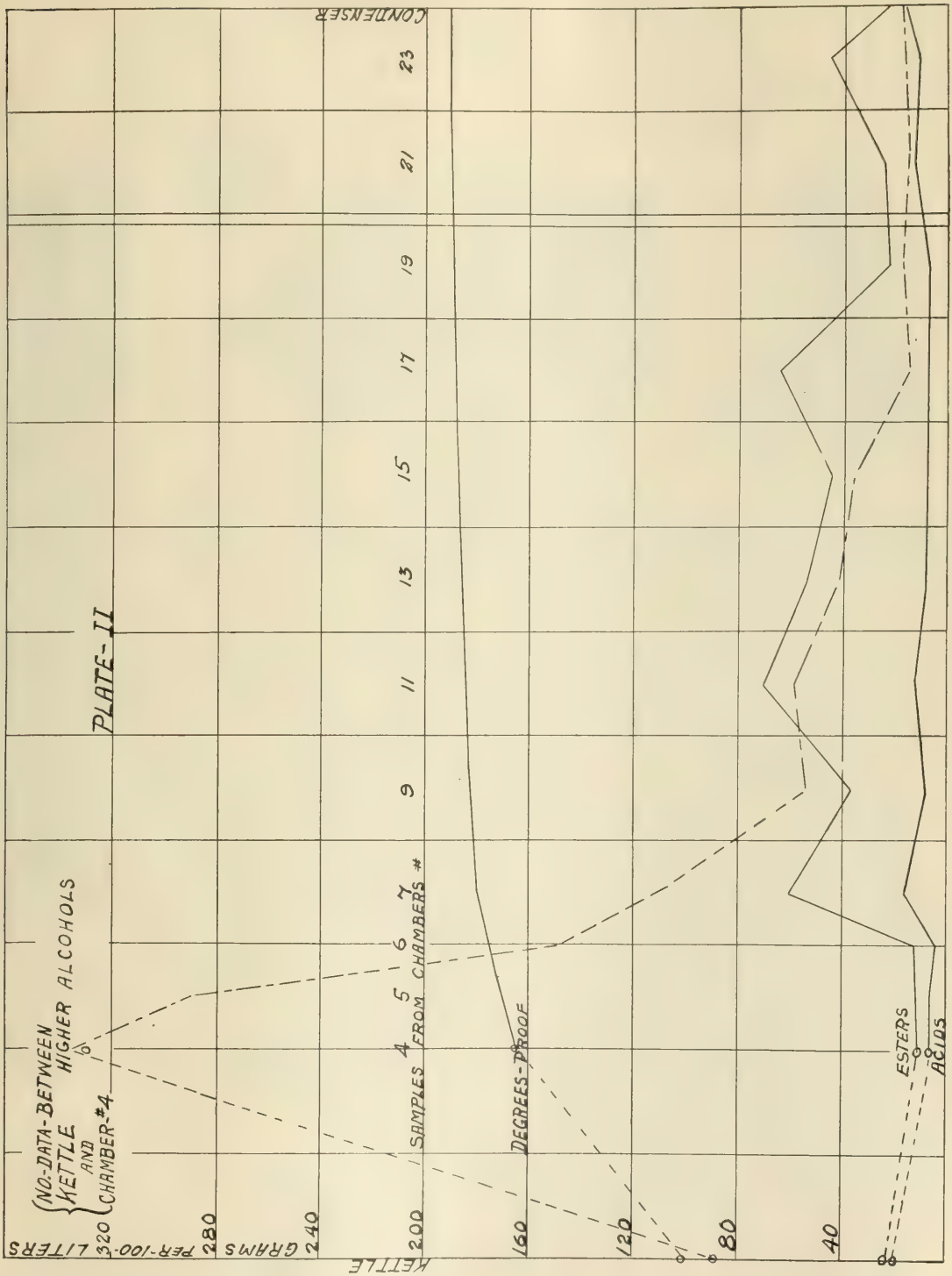


PLATE-II
CONDENSER
KETTLE
SAMPLES FROM CHAMBERS #
DEGREES-PROOF
GRAMS PER-100-LITERS
(NO.-DATA-BETWEEN KETTLE AND CHAMBER-#4
HIGHER ALCOHOLS
ESTERS
ACIDS
320
280
240
200
160
120
80
40
0
4
5
6
7
9
11
13
15
17
19
21
23

SAMPLES FROM ALCOHOL DISTILLATION.

Grams per 100 liters (based on original sample). Beer still samples.

Lab. No.	Description.	Gallons.	Proof. Degrees.	Acids.	Esters.	Higher alcohols.	Aldehydes.	Furfurol
36814	Distillate No. 1	2000	101	21.6	22.3	100.2	120	0.0
36815	Distillate No. 2	2000	101	21.6	22.3	86.2	120	0.0
36816	Mixture of above after filtering through charcoal average of kettle	4000	101	20.4	22.3	86.2	125	0.0

SAMPLES FROM COLUMN.

Lab. No.	Sample No.	Description.	Time taken.	Proof. Degrees.	Acids.	Esters.	Higher alcohols.	Aldehydes.	Furfurol.
36817	1	Low wines	10.13 A.M.	185	32.6	70.4	47.5	6000	0.0
36818	2	Low wines	10.25	185	18.0	79.2	38.7	6400	0.0
36819	3	Low wines	10.45	180	27.6	82.7	36.0	4800	...
36820	4	Heads	11.01	185	54.0	78.6	32.0	2320	...
36821	5	Heads	11.45	187	48.0	71.6	19.4	2200	...
36822	6	Heads	12.35	189	45.6	45.2	19.4	800	...
36823	7	Heads	1.15 P.M.	190	63.6	38.2	19.4	426	...
36824	8	Heads	2.15	191	60.0	31.1	19.0	370	0.0
36825	9	Heads	3.15	191	54.0	25.8	17.6	96	0.0
36826	10	Heads	4.15	191	42.0	24.1	22.9	42	0.0
36827	11	Heads	5.40	191	36.0	17.6	19.4	13	0.0
36828	12	Heads	6.40	191	32.4	21.1	17.6	7.2	0.0
36829	13	Middle run	8.45	191	15.6	21.1	16.3	1.8	0.0
36830	14	Middle run	2.00 A.M.	191	12.0	19.4	18.0	1.1	...
36831	15	Middle run	7.30	191	8.4	24.6	16.3	1.2	0.0
36832	16	Tails	8.00	190	9.6	28.2	15.0	1.3	...
36833	17	Tails	9.13	190	8.4	24.6	21.1	1.3	0.0
36834	18	Tails	10.10	190	3.6	14.1	25.0	1.3	...
36835	19	Tails	11.05	187	9.6	28.2	122.3	trace	0.0
36836	20	Low wines	11.50	182	16.8	17.6	840.0	1.0	...
36837	21	Low wines	12.06 P.M.	172	10.8	22.9	2650.0	1.0	0.0
36838	22	Low wines	12.30	...	8.4	40.5	16.3%	2.2	...
...	..	Fusel oil	12.38 Begins						
...	..	Fusel oil	1.00 Ends						
...	..	Water-clean out							

SAMPLES FROM CHAMBERS OF COLUMN.

Grams per 100 liters (original samples).

Lab. No.		Proof.	Acids.	Esters.	Higher alcohols.	Aldehydes.	Furfurol.
36816	Average of kettle when charged.	101%	20.4	22.3	86.2	125	0.0
Lab. No.	No. of chambers from bottom.						
36855	4	164.4	6.0	10.6	336.2	faint trace	0.0
36856	5	170.8	6.0	12.3	292.9	faint trace	0.0
36857	6	174.4	4.8	12.3	148.8	faint trace	...
36858	7	180.4	15.6	61.6	111.0	faint trace	...
36859	9	183.0	8.4	35.2	54.3	faint trace	...
36860	11	184.8	13.2	70.4	58.1	faint trace	...
36861	13	186.0	8.4	52.8	41.4	faint trace	0.0
36862	15	187.2	7.2	44.0	35.2	faint trace	...
36863	17	188.4	7.2	65.1	15.0	faint trace	...
36864	19	189.1	7.2	22.9	17.6	faint trace	...
36865	21	190.2	13.2	24.6	14.1	faint trace	...
36866	23	190.7	10.8	44.0	17.6	faint trace	0.0
36829	at condenser finished alcohol	190.8	15.6	21.1	16.3	1.8	0.0

SAMPLES FROM CHAMBERS OF COLUMN.

Grams per 100 liters calculated to 100 proof.

Acids.	Esters.	Higher alcohols.	Aldehydes.	Furfurol.
20.2	22.1	85.4	124	0.0
3.6	6.4	204.6	0.0	0.0
3.5	7.2	171.5	...	...
2.7	7.1	85.3	...	...
8.6	34.1	61.5	...	...
4.6	19.2	29.7	...	...
7.1	38.0	31.4	...	...
4.5	28.4	22.3	...	...
3.8	23.5	18.8	...	...
3.8	34.5	7.9	...	...
3.8	12.1	9.3	...	...
6.9	12.9	7.4	...	...
5.6	23.0	9.2	...	...
8.2	11.1	9.0	...	...

proportion distilled at less than 128°, proving that the Allen-Marquardt method estimates only about 50 per cent. of the total higher alcohols present in *this* particular sample.

Preliminary fractionation of a sample of salable fusel oil from this distillation proves it to contain at least 75 per cent. of amyl alcohol, boiling at 128°–132°; therefore, as the Allen-Marquardt method estimates practically all of this alcohol, then the proportion of the lower boiling point, higher alcohols, in this sample 36838 must be greater than in the marketable fusel oil.

On account of the small samples taken and the limited time available, I can not at this time complete the work along these lines, but hope to carry it to completion at some future time.

PURE LINSEED OIL.

By E. J. SHEPPARD.

Received October 20, 1911.

The majority of writers on the subject of linseed oil state that linseed invariably contains admixed seeds and straw as impurities; but, with the exception of the article by Ketel and Antusch,[1] there is no data

[1] *Z. angew. Chem.*, **1896**, 581.

available of the precise effect of these impurities on the constants of the oil. Church, however, calls attention to the injurious effect of weed seeds on the color of the oil. The following investigation was undertaken in order to establish the exact influence of these impurities on the oil.

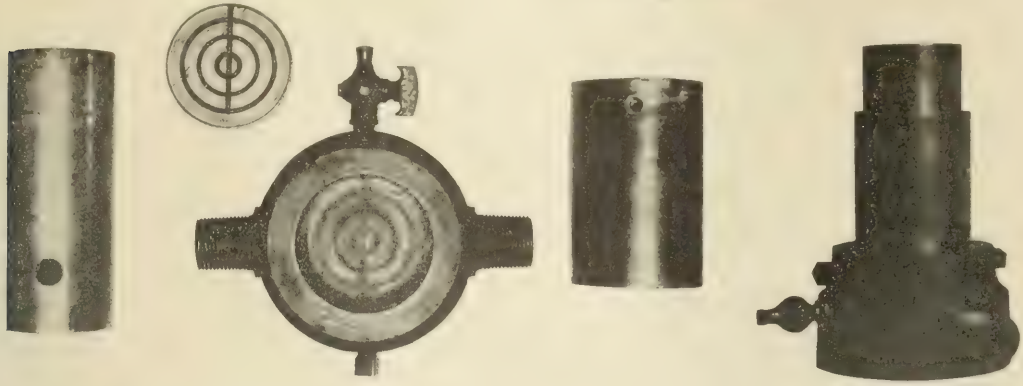


Fig. 1.

It was thought best to obtain the oil by the pressure method rather than by the extraction method as employed by Ketel and Antusch. The accompanying drawings and photographs (Fig. 1) show the details of construction of the special press designed and built for this purpose by Professor A. H. Sabin: *A*, in Fig. 2, is a cast-iron base. *B* is a piece of steel tubing. *C*, in Fig. 3, is a perforated steel plate, the grooves of which serve as channels for the oil; in use it is placed with grooves down. *D* is a solid piece of shafting; this serves as a piston. In practice,

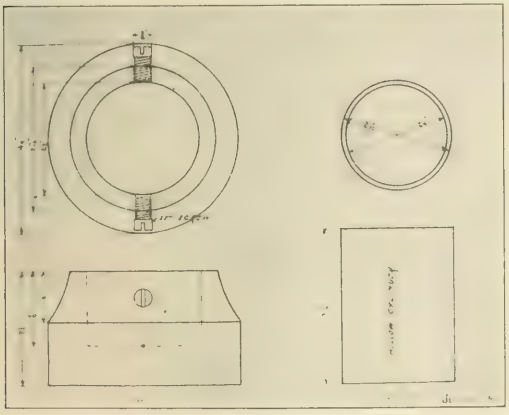


Fig. 2.

a piece of wire gauze fitting inside of *B* is placed on *C*; this prevents the charge from wedging in the holes of the plate *C*.

Samples of seed, as used for pressing, were taken at an oil-mill together with samples of the oil pressed therefrom—Samples A. Portions of the seed as received were pressed in the special press and gave samples B. About 300 grams of the seed were completely freed of impurities by screening and by hand picking. Portions of the clean seed were analyzed and the data obtained are shown in Table I. On pressing the clean seed, oil sample *C* was obtained.

Samples 1, 2, 3 and 4 are considered as representative of seed used for crushing in this country; 5, 6 and 7 were imported in a small quantity, but are believed to be representative—no authentic factory samples of oil could be obtained. The average weight per seed was obtained on 4000 full-sized seeds; these were afterward used for the specific gravity determination.

TABLE I.

Seed.	Oil. Per cent.	Sp. gr. 15.5° C. 15.5° C.	Average weight per seed. Mg.	Oleaginous impurities. Per cent.	Non-oleaginous impurities. Per cent.	Oil in total impurities. Per cent.
1—American	39.67	1.1388	4.61	1.50	1.69	10.0
2—American	39.40	....	4.53	1.01	1.05	..
3—La Plata	36.98	1.1415	5.58	0.58	5.64	14.1
4—Calcutta	40.82	1.1326	5.41	4.85	5.03	14.9
5—Bombay	41.23	1.1182	7.88	0.81	2.80	..
6—S. Russia (Kertch)	39.11	1.1375	5.74	5.05	1.71	..
7—N. Russia (Riga)	36.95	1.1458	4.19	3.31	1.97	.

The per cent. of oil was obtained by the extraction method. The percentages of impurities refer, of course, to the amounts present in the seed as received. In the case of the Calcutta seed, the percentage of total impurities is a trifle high, as the average of 11 recent samples was 6.90 per cent.—containing 15.1 per cent. oil. The oil in the clean Calcutta seed averaged 41.01 per cent.

Andes[1] is evidently in error on the average weight of a seed. Wijs' figures[2] on the amount of impurities present in various seeds are correct in some cases. It is a remarkable fact that the percentages of impurities in the Calcutta and Russian seeds do not confirm the statements of most writers on the subject that "Calcutta and Baltic seeds are freer from foreign seeds than the American and La Plata seeds, and that, consequently, the oils are of better quality." Apparently, this prejudice regarding the presence of

[1] "Drying Oils," page 58.
[2] Andes, *Ibid.*, page 318.

foreign seeds in commercial American linseed is unfounded.

In preparing the oil, the seed was ground in a coffee-mill, placed in a Mason jar and steam introduced, the jar covered and placed in a steam oven for 2 hours. On removal, the meal was at once packed in cloth and placed in the press, the piston inserted and, using the screw of a filter-press, pressure was applied, the oil draining through the outlet tube into a bottle wired to the press. The first test-run showed that only slightly more oil was left in the cake than in regular factory practice.

Table II contains the analytical results obtained on the oils. In all cases, the oil was filtered through paper before making a determination. Sample 2A is an extraction process oil; all the other factory samples are oils manufactured by the old process hydraulic method.

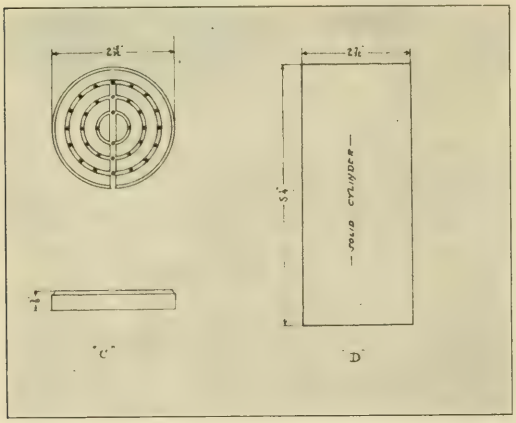


Fig. 3.

Analyses: 1A and 2A give the results obtained recently on the factory samples of oil, while $1A_1$ and $2A_1$ are the results obtained two years ago on the same samples, indicating that no change in the constants determined took place in the oils. Samples 1B, 1C and 2C were pressed in the laboratory from seed kept $2^1/_2$ years in closed Mason jars.

TABLE II.

No.	Oil.	Sp. gr. 15.5° C. 15.5° C.	Ref. index at 25° C.	Iodine No. (Hanus.)	Color.
1	American—A	0.9346	1.4802	187.5	yellow
	American—A_1	0.9347	1.4800	187.9	yellow
	American—B	0.9347	1.4800	187.6	yellow
	American—C	0.9346	1.4800	187.5	yellow
2	American—A	0.9330	1.4800	185.9	yellow
	American—A_1	0.9331	1.4797	186.1	yellow
	American—C	0.9330	1.4800	186.5	yellow
3	La Plata—A	0.9316	1.4782	171.4	green
	La Plata—B	0.9316	1.4782	171.8	green
	La Plata—C	0.9317	1.4783	171.1	orange
4	Calcutta—A	0.9329	1.4790	178.9	yellow
	Calcutta—B	0.9327	1.4792	179.3	yellow
	Calcutta—C	0.9327	1.4793	180.5	yellow
5	Bombay—C	0.9316	1.4790	176.9	yellow
6	S. Russian (Kertch)—C	0.9317	1.4795	177.0	orange
7	N. Russian (Riga)—C	0.9354	1.4815	196.4	green

So far as the writer knows, no figures have been published giving the analysis of oils from picked seed, with the exception of Thomson and Dunlop[1] who obtained 205.4 as the iodine no. on oil from picked Riga seed, but they used the Wijs method. Ketel and Antusch[2] give data of the effect on the oil of varying amounts of dotter and rape seeds added to clean linseed, but they used the extraction method for obtaining the oil; while, in a later article[3] they admit the possibility of a lower iodine no. in extracted oil, they state that to their knowledge this has never been actually tested. It may also be mentioned that the amounts of dotter and rape seeds added are considerably out of proportion to those actually present in the commercial seed examined.

Mastbaum states[4] that "expressed oil has a higher iodine no. than extracted oil." The comparative analysis of 2A and 2C would seem to indicate, however, that this is not necessarily so.

It is worthy of note that high percentages of non-oleaginous and low percentages of oleaginous impurities, as in the La Plata seed, do not affect the constants, but do affect the color of the oil. On the other hand, with the Calcutta seed, the variation in iodine no. can hardly be due to experimental error—more likely to the high per cent. of oleaginous impurities—whereas the color is only slightly affected. The green color of the Riga oil must be due to some coloring matter present in the seed itself.

The typical analyses quoted in Table II fall well within the limits set by Wijs when the usual difference between the Hanus iodine no. and the Wijs no. is considered.

From a consideration of the results it appears that

1. Oil pressed from clean linseed does not differ materially from commercially pure linseed oil.

2. The dark green color of the La Plata oil is due to the non-oleaginous impurities.

3. A high per cent. of oleaginous impurities does not affect the color appreciably, but does affect the iodine no. slightly.

4. The technical manufacture of oil by the extraction process does not lower the iodine no.

5. The constants of the oil pressed from the seed which had been kept $2^1/_2$ years in a closed container do not appear to be affected by the aging of the seed.

LABORATORY NATIONAL LEAD COMPANY,
BROOKLYN, N. Y.

ARSENIC IN GLASS.

By S. R. SCHOLES.

Received November 13, 1911.

In Hovestadt's excellent work on "Jena Glass" arsenic oxide (As_2O_5) is listed among the constituents of many of the glasses described, in quantities of from 0.2 to 0.4 per cent. The English edition of this book contains a note by Everett, the senior translator.

[1] *Analyst*, **1906**, 282.
[2] *Loc. cit.*
[3] *Z. angew Chem.*, **1897**, 210.
[4] *Ibid.*, **1896**, 719.

who takes exception to this view, arguing that the pentoxide would be reduced at the glass-making temperature. Rosenhain, author of "Glass Manufacture," supports the latter opinion, and adds that he believes very little arsenic remains in the glass at all. It seemed of interest, therefore, to study this question from the analytical standpoint, by examination of the glass itself. Some unexpected results were obtained.

Two varieties of glass were analyzed for arsenic: No. 1, a soda-baryta glass, of fairly high alkali-content; No. 2, a potash-lead glass, used for cut-glass ware. In No. 1, the arsenious oxide put into the batch, or raw materials, was between 0.3 and 0.5 per cent. of the glass produced, while in No. 2 it was approximately 0.45 per cent. In both these batches, potassium nitrate was used in considerable quantity, and in No. 2 red lead was one of the main constituents, so that there was abundant opportunity for the initial oxidation of the arsenic to the pentavalent condition. The method used for determining the percentage and state of oxidation of the arsenic remaining in the glass was as follows:

Samples of glass, powdered to pass a 40-mesh sieve, were weighed into a platinum dish and treated with 15–20 cc. of hydrofluoric acid, added in three portions. When reaction had ceased, 20 cc. of 30 per cent. sulphuric acid were added, and the mixture evaporated on a water-bath until hydrofluoric acid fumes ceased coming off. It was then rinsed into a beaker, making a total volume of 40 cc., and arsenic acid determined by titration after the manner described in Sutton's "Volumetric Analysis." In the case of the lead glass, the solution was filtered before the addition of potassium iodide, to remove the lead sulphate and avoid formation of lead iodide. After titrating with thiosulphate, the solution was nearly neutralized with sodium carbonate, 20 cc. of a saturated solution of sodium bicarbonate were added, the arsenious acid was titrated with iodine, and the arsenious oxide originally present determined by difference. The standard solutions used were twentieth-normal. Blank determinations showed that the reagents contained no measurable quantity of arsenic. The data obtained are tabulated below.

Glass. No.	Grams sample.	Cc. $N/20$ thio-sulphate.	Cc. $N/20$ iodine.	As_2O_5.	As_2O_3.	Per cent. As_2O_5.	Per cent. As_2O_3.
1	6.60	9.0	9.1	0.02587	0.0003	0.39	0.00
1	4.82	4.2	5.1	0.01207	0.0022	0.25	0.05
2	4.25	5.9	6.6	0.01696	0.0017	0.40	0.04
2	7.73	9.6	9.6	0.02760	0.0000	0.36	0.00
2[1]	6.00	8.6	8.6	0.02472	0.0000	0.41	0.00

These results indicate that a great part of the arsenic used in glass-making remains in the glass as the higher oxide, probably as arsenate of soda or potash. This is somewhat surprising, in view of the properties attributed to arsenic in justification of its use. It is expected to volatilize, aiding in the mixing of the batch as the latter melts. Moreover, it is said to have an oxidizing effect, but the fact that the arsenious oxide originally employed appears finally in the glass with a gain of oxygen does not bear out this belief. On the contrary, it seems that the use of arsenic must reduce the available oxygen of the batch. At least in cases where nitrates are present and the melting carried on in closed pots, as in the manufacture of the glasses here examined, the value of the arsenic, if any, obviously lies in neither its volatilizing nor its oxidizing powers.

[1] Sample fused with sodium carbonate and dissolved in sulphuric acid

The glass used and the data concerning it were furnished by one of the glass companies of this vicinity.

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THE DETERMINATION OF CHROMIUM AND ITS SEPARATION FROM VANADIUM IN STEELS.

By J. R. Cain.

Received November 10, 1911.

While attempting, recently, to determine chromium in chrome-vanadium steels, difficulties with some of the usual methods were encountered. If a steel containing chromium as chromate and vanadium as vanadate is titrated against ferrous solutions, using ferricyanide to indicate the point at which all the vanadium and chromium are reduced and an excess of titrating solution is present, there is sometimes an indefinite end-point, because as soon as some vanadium is reduced to the vanadyl condition this reacts with the ferricyanide indicator, reducing it to ferrocyanide which then gives the usual color with the ferric salts present.[1] An experienced operator can oftentimes judge the end-point sufficiently closely for practical work, but the difficulty increases with increasing vanadium, and it is almost always necessary to run blanks of various kinds, increasing to that extent the uncertainties of such methods. If the excess of ferrous solution is titrated back with permanganate some correction is also necessary for chromium oxidized by permanganate.[2] If in the preliminary oxidation of the vanadium and chromium, any manganese dioxide separates, as where potassium permanganate or potassium chlorate are used, some chromium may be, and often is, carried down by the manganese.[3] If, in order to separate vanadate from chromate, the nitric acid solution of the steel (with or without preliminary ether extraction of most of the iron) is poured into excess of sodium hydroxide solution and boiled, usually an appreciable amount of chromium goes into the filtrate with the vanadium. Many methods take no account of this chromium. The amount so lost increases with the manganese in the steel and the time of boiling, the manganese being converted in part to peroxide and this, in the strongly alkaline solution, oxidizing the chromium to chromate.[4]

Many careful tests having shown that chromium in

[1] Cain, This Journal, 3, 476 (1911); other references will be found here.

[2] Cain, *loc. cit.*

[3] Arnold and Ibbottson, "Steel Works Analysis," 3rd Ed., p. 180, also Cain, *loc. cit.*

[4] Cain, *loc. cit.*

much larger amount than the usual commercial steels carry can be precipitated completely in a few minutes by boiling the nearly neutralized (ferrous) solution of the steel with barium carbonate, cadmium carbonate, zinc oxide or magnesium oxide, it was decided to base a method for determining chromium on one of these methods of separation from iron. Probably the reason why such separations have not come into more general use is because practically all writers have directed to make the carbonate or oxide precipitation in the cold, which requires many hours' standing and is even then sometimes incomplete. The work done here has shown that but ten or fifteen minutes' boiling, with proper precautions, is all that is ever necessary, the filtrates being free from even traces of chromium (or vanadium).

Noyes and Bray[1] have given conditions for completely precipitating chromates in the presence of vanadates which make possible a good separation of the two elements. The work here having completely confirmed their results, this separation was incorporated in the method.

DESCRIPTION OF THE METHOD.

Dissolve in a covered 300 cc. Erlenmeyer flask an amount of drillings, which will give not to exceed 6 or 7 centigrams of chromium, using about 10 cc. of concentrated hydrochloric acid per gram of steel. The concentrated acid (specific gravity 1.20) seems to dissolve the steel much more readily than a diluted acid. When no more hydrogen is given off, dilute to 100 or 150 cc. with hot water, nearly neutralize with saturated sodium carbonate solution, add barium carbonate emulsion in slight excess, place on the hot plate and boil vigorously ten or fifteen minutes, with small additions of the barium carbonate emulsion every two or three minutes. The flask should be kept covered during all operations so as to exclude air as completely as possible. Too great an excess of barium carbonate should not be used, as this increases the difficulty of extracting the chromium in the subsequent fusion. An excess of a gram or two is the most that should be present. Remove the flask from the plate, let the precipitate settle, and filter at once on a 11 cm. white label No. 589 filter, washing twice with hot water. These operations should be carried out rapidly and without delay. Place the filter and precipitate in a sufficiently large platinum crucible, burn off the filter, add 2 grams of sodium carbonate and about $^1/_4$ gram potassium nitrate, and fuse for 20 minutes. Support the inverted and inclined crucible on a glass triangle which has glass legs about $^3/_4$ inch long fused to its corners for supports, place on the bottom of a 250 cc. beaker, cover it with boiling water and digest a few minutes until the fusion is disintegrated. Filter into a flask, add 1 or 2 cubic centimeters of hydrogen peroxide to the filtrate and boil for five or ten minutes to destroy the excess of peroxide. Cool, transfer to a 250 or 300 cc. separatory funnel, add a slight excess of nitric acid (1–1), and shake vigorously a few minutes, allowing the liberated carbon dioxide to escape by inverting the separatory funnel and opening the stopcock. Transfer to a 250 cc. beaker, just neutralize with sodium hydroxide solution, and then add nitric acid (1–1), 2 cc. for each 100 cc. of solution. Add 20 cc. of a 20 per cent. lead nitrate solution to the cold solution, stirring vigorously. The precipitate settles quickly. It is filtered on asbestos, and washed three or four times with cold water. The asbestos mat is transferred to a beaker or flask, and the lead chromate decomposed with hot hydrochloric acid (1–4). The solution is cooled, the volume made up to 150 or 200 cc. and it is titrated against approximately N/10 ferrous sulphate solution with ferricyanide as outside indicator. Or, if desired, an excess of the ferrous sulphate solution is added and the excess titrated back against bichromate. The standard iron solution should be compared with bichromate or permanganate on the day it is used. Table I gives results obtained with synthetic solutions and with the chrome-vanadium standard steel of the Bureau of Standards. The synthetic solutions were made by adding the chromium from a carefully standardized bichromate solution and the vanadium from a sodium vanadate solution to the hydrochloric acid solution of a vanadium and chromium free steel.

TABLE I.

No. of expt.	Iron present. Grams.	Vanadium present.	Chromium present.	Chromium found.	Difference.
1	1	0.0012	0.0140	0.0137	—0.0003
2	1	0.0024	0.0280	0.0277	—0.0003
3	1	0.0024	0.0420	0.0420	0.0000
4	1	0.0036	0.0560	0.0558	—0.0002
5	1	0.0048	0.0700	0.0700	0.0000
6	1	0.0060	0.1120	0.1122	+0.0002
7	1	0.0120	0.1680	0.1685	+0.0005
8	1	0.0180	0.2800	0.2805	+0.0005
9[1]	4	..	..	0.0536	..

NOTES AND PRECAUTIONS.

Numbers 6, 7 and 8 of Table I show that very large amounts of chromium can be completely precipitated by the barium carbonate method carried out as above described. However, if the amount of chromium exceeds that recommended in the method described herein, it cannot be readily extracted by 2 grams of sodium carbonate, particularly if too great an excess of barium is present. The amount of sodium carbonate used was governed by the directions of Noyes and Bray[2] who state that, for a successful separation of chromium, not too much sodium nitrate should be present. The separations described herein were made in a volume of 250 cc., and inasmuch as 2 grams of sodium carbonate were used for fusions, the resulting sodium nitrate concentration was about 1.3 grams per 100 cc. The filtrates were tested for chromium by removing the excess of lead with sulphuric acid, filtering, concentrating to about 10 or 15 cc. and making alkaline with sodium hydroxide. No color indicative of chromate was ever obtained, even after adding a little hydrogen peroxide and boiling to

[1] *Technology Quarterly*, **21**, 14 (1908).

[1] Chrome-vanadium standard: 4 determinations; each gave 1.34 per cent. Average of results of coöperating analysts: per cent. chromium 1.36, per cent. vanadium 0.204.

[2] *Loc. cit.*, p. 48, Note 4.

oxidize any chromium that may have been reduced. Possibly the larger amounts of chromium could have been completely extracted by one fusion, had more sodium carbonate been used, but the manipulation is then less convenient; moreover, with the usual range of chromium content in commercial steels one need never work with more than 7 or 8 centigrams to secure an accurate determination.

The boiling with hydrogen peroxide in alkaline solutions before precipitation with lead nitrate is done in order to destroy any nitrite formed during the fusion. If this were present when the solution is acidified, the resulting nitrous acid would possibly reduce some chromium or vanadium. Five minutes' boiling will insure destruction of the excess of peroxide if only 2 or 3 cc. of the usual 3 per cent. solution are used. The hydrogen peroxide should be completely removed before acidifying, inasmuch as it reduces chromic acid.[1]

The freeing of the solution from carbon dioxide is an important step, for if this is not done, the precipitate does not settle out rapidly and is not so easy to filter; shaking in a separatory funnel, as described, is a convenient way of accomplishing this.

The solutions containing the chromium, after titration, were treated with enough sulphuric acid to precipitate the lead, which was filtered off and washed with dilute sulphuric acid. The filtrates were evaporated on the hot plate until free from hydrochloric acid and then electrolyzed with a mercury cathode[2] until free from iron and chromium. The solution in the electrolyzing apparatus was then tested for vanadium by hydrogen peroxide, none being found in most cases and in others only traces, showing that the separation under the conditions given is practically perfect. It is well to examine the insoluble from the fusion for chromium by again fusing it with sodium carbonate and potassium nitrate. The solution from the second fusion is almost invariably colorless when working under the conditions herein recommended. Should there be a slight yellow color, however, the chromium causing it can be estimated colorimetrically. A determination of chromium can be made easily in $1^1/_2$ hours.

CONCLUSIONS.

1. Sources of error in some of the usual methods for determining chromium in chrome or chrome-vanadium steels, which limit the accuracy of the results, are described.

2. The precipitation of chromium from solutions of steels and its separation from practically all the iron can be effected quickly and easily by boiling with a number of precipitants, herein described.

3. The chromium may be readily extracted from the precipitates by fusion, and separated from vanadium by precipitating as lead chromate, under the conditions prescribed.

BUREAU OF STANDARDS.
WASHINGTON.

[1] Perchromic acid is first formed, but is rapidly decomposed.
[2] Cain, *loc. cit.*

THE BISMUTHATE METHOD FOR MANGANESE.

By D. J. DEMOREST.

Received October 20, 1911.

There seems to be considerable misapprehension as to the effect which chromium has upon the bismuthate method for manganese. Thus it has been stated that chromium affects the results for manganese by this method. If, however, the method is properly carried on, the chromium has no influence. It is true that the bismuthate oxidizes some of the chromium to chromic acid, and this is titrated along with the manganese if the manganese is titrated by adding an excess of ferrous sulphate and then titrating the excess with permanganate. This is not the proper way. If the permanganic acid is titrated directly with sodium arsenite until the pink color disappears, the chromic or vanadic acids which may be present do not interfere at all and the results are accurate.

To show this, the vanadium steel standard issued by the Bureau of Standards was analyzed for manganese with and without the addition of chromium. The Bureau gives 0.669 per cent. as the manganese in the steel. The following results were obtained.

Without adding chromium.	With 3 per cent. chromium added as $K_2Cr_2O_7$.
0.666	0.669
0.666	0.666
0.666	0.671
Another steel was run in the same way obtaining:	
0.468	0.468

The acid open-hearth steel standard issued by the Bureau of Standards, and for which the Bureau gives 0.407 as their average, and the average by the cooperative chemists as 0.412 was analyzed with and without 3 per cent. Cr. The results were 0.403 per cent. Mn without, and 0.405 per cent. Cr with 3 per cent. chromium. Another sample gave 0.489 per cent. without addition of Cr or V and 0.488 per cent. with the addition of 3 per cent. Cr and $1^1/_2$ per cent. V.

The method as used in this laboratory is as follows: One gram sample is dissolved in 45 cc. of water and 15 cc. HNO_3 (sp. gr. 1.42) and the solution boiled until nitrous fumes are gone. After cooling a little some "bismuthate" is added, a little at a time, until the resulting permanganic acid or manganese dioxide persists after a few minutes' boiling. Now KNO_2 is added to dissolve the MnO_2 and the solution is boiled a few minutes to expel nitrous fumes. It is then cooled to tap water temperature. When cold, bismuthate is added a little at a time, while the solution is shaken, until about $^1/_4$ gram has been added. After settling a moment the solution is filtered through asbestos on glass wool (for speed) and the asbestos washed well. Then sodium arsenite is run in from a burette until the pink tinge just disappears. There should not be a brownish color at the end. If there is, it indicates insufficient acid.

The arsenite is made by adding to $2^1/_4$ g. As_2O_3 in a beaker a hot solution of Na_2CO_3 until the As_2O_3 dissolves. It is then diluted to $2^1/_2$ liters.

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SALT-RISING BREAD AND SOME COMPARISONS WITH BREAD MADE WITH YEAST.[1]

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Received October 12, 1911.

Bread is made light and porous by two methods of aeration. The oldest of these and the one, which is most extensively used at present, involves a process of fermentation, in which various microörganisms produce the gas necessary to raise the bread; by the other method it is given a porous character, either by forcing carbon dioxide under pressure into the dough while it is being mixed, as is done in making aerated bread, or by mixing with the other ingredients certain chemicals, which, when they come in contact with the water used in making the dough, evolve gas, either immediately upon mixing the bread or later when it becomes hot during the process of baking.

The method of preparing bread with the aid of yeast has been extensively investigated and the function of this microörganism in bread is now thoroughly understood. By means of the saccharifying enzyme, diastase, which is present in flour, a part of the starch is converted into sugar, which as well as that normally present in flours and that added in making the dough either as sugar in some form or other, or malt extract, is partly converted by the yeast into alcohol and carbon dioxide which aerates the bread.

Another type of bread, involving a process of fermentation, the so-called salt-rising bread, is made by many housewives and bakers, particularly in the south and is not so thoroughly understood and offers far greater difficulties in its preparation. In its preparation there is added neither yeast nor a portion of fermented dough from the previous baking, as is done in making certain kinds of rye bread and a type of white bread as well. In fact there is nothing added that can be called leaven, and each day's baking is dependent upon a new and independent spontaneous fermentation. The method that is commonly employed is as follows: Cornmeal, salt and soda are thoroughly mixed and stirred into enough hot milk or water, often boiling, to make a batter of the consistency of corn meal mush. This batter or "emptyings," as it is commonly called, is kept in a warm place 15 to 20 hours or until it becomes light and shows the evolution of gas, and is then mixed with flour and water to make a slag sponge. The sponge is allowed to come up well which may take from one to three hours, and is then mixed with the remainder of the ingredients to make a dough of the usual stiffness. The dough is allowed to stand not longer than an hour but is usually moulded into loaves immediately upon mixing. After it has risen to the degree of lightness desired, it is baked in the usual way.

The literature on the subject indicates that the theory of the leaven in this bread is very incompletely worked out and that there are conflicting views both in regard to the nature of the organism or organisms involved and to its source.

In reference to salt-rising bread Margaret Mitchell[1] says: "When a brew is prepared, but no stack yeast or raw dough is added, it will still be found that in time the mixture will ferment if kept warm. This spontaneous fermentation is due to the fact that yeast spores, when dried, are very light, and are blown about so that they are present almost everywhere. These floating spores may be those of the household yeast, or those of 'wild' yeasts which are common, for instance, in drying fruit, etc., but which are not often cultivated. The spores can enter the brew from the air or from utensils used in mixing. When accidentally planted they grow, as any yeast would, and produce fermentation. Along with the 'wild' yeast obtained in this method of making bread, there are usually also obtained a large number of bacteria, which form bodies of characteristic odor and flavor in the course of their fermentation; and to this is due the peculiar odor and flavor of the salt-rising bread."

She says further: "The uncertainty of this method of making bread is one of its disadvantages, but when it is made, often in the same place the 'wild' yeast most successful in raising this kind of bread is apt to be more abundant in the air, utensils, etc., than other 'wild' yeasts."

Professor F. C. Harrison[2] says the following: "There is another method of making risen bread, that is the method called 'salt-rising.' It is the result of a spontaneous fermentation, and is therefore a matter of chance whether good bread will be produced, although in places where such bread has been made for some time there is less likelihood of failure, as the utensils and air of the rooms in which the bread is made contain large numbers of the desirable germs." Dr. E. H. S. Bailey[3] describes the process as follows: "The salt-rising process depends on preparing a favorable medium in which the yeast germs will grow, and then allowing them to get into the dough from the air, or from the ingredients used in making the sponge. The bread is started by the use of flour, or cornmeal, warm milk, and salt. The meal begins to ferment after a short time, if kept in a warm place, but the fermented material will not have the same taste and odor as the sponge from yeast, as various 'wild' yeasts are sure to be present. It is probable that lactic and butyric fermentation also take place to some extent. Although salt, in any quantities above 1.4 per cent., retards alcoholic fermentation, yet as it even to a greater extent retards the growth of foreign ferments, such as lactic and certain 'wild' ferments, it is probable that its addition is an advantage, on the whole, if this method of fermentation is used. Salt-rising bread is finer grained than yeast bread and has a peculiar and characteristic odor, which is due, no doubt, to the lactic fermentation which has taken place."

Helen W. Atwater[4] describes it thus: "The so-called 'salt-rising' bread is interesting as an illustration of self-raised bread. In it the ferments originally

[1] This work was done under the Fellowship established in the University of Kansas, by the National Association of Master Bakers, and the results have in part been made public in papers read in conventions, and through a series of articles in *The Bakers' Review*.

[1] *U. S. Department Agricultural Bulletin*, **200**, p. 45.

[2] *Ont. Agricultural Bulletin*, **118**, p. 16.

[3] "Sanitary and Applied Chemistry," p. 168.

[4] U. S. Dept. Agr., *Farmers' Bulletin*, **389**, p. 21.

present or acquired from the air produce the fermentation which leavens it. To make it warm milk and cornmeal are mixed together into a stiff batter which is left at blood-heat until the whole mass is sour—that is, until the ferments present have produced fermentation throughout. Next a thick sponge is made of wheat flour and hot water in which a little salt has been dissolved. This sponge and the sour batter are thoroughly kneaded together and set in a warm place for several hours. The leavening action started in the batter spreads through the dough and produces a light, porous loaf, which many persons consider very palatable. Such a bread is comparatively free from acidity, as the presence of the salt hinders undesirable acid fermentation."

P. G. Heinemann and Mary Hefferan,[1] in an investigation of salt-rising bread, isolated a bacillus which agrees in morphology, staining properties and other cultural characteristics with *B. bulgaricus*. In a stain from the mixture of cornmeal, milk, salt and soda the bacilli present showed a granular appearance, but after growing in milk they stained uniformly. These bacilli, the authors failed utterly to isolate by plating on ordinary laboratory media, but they were readily isolated if cultivated in milk at 37° C. or if plated with milk-agar. In milk the pure culture forms a soft creamy coagulum which does not separate from the whey. After 14 days the milk showed an acidity of 1.65 per cent. and the authors think that the milk is a necessary part as without it the bacillus is unable to produce the acid necessary to liberate the carbon dioxide from the added soda. By inoculating sterile milk with cornmeal it was demonstrated that the origin of the organism was the cornmeal and not the milk.

Erbert J. Clapp,[2] in a paper on salt-rising bread, tells of the extreme difficulties encountered in making it and enumerates the conditions and ingredients that he finds important. It is his experience and that of bakers as well that success depends to a large extent upon the king of cornmeal used. Kiln-dried meal is found to give poor results. Best of all he finds coarse meal, "hulls, shucks and all," as he describes it. The hulls and shucks are strained out, however, in making the sponge. He enumerates potatoes which are not generally used as one of the essential ingredients, but says that river bottom potatoes which are high in moisture and low in starch do not give satisfactory results.

Mr. Clapp's formula differs also from the one ordinarily given in that it includes ginger as one of the essential ingredients; milk, on the other hand, is not used at all and he says its use is to be avoided entirely.

He emphasizes the fact that it is important to scald the vessels used in making the bread and to guard against souring. The evolving gas he observed would burn (explode) when a lighted match is applied which he attributes to the generation of alcohol.

It is evident that while there are conflicting views in the above references, there are also some points of agreement. All of the writers agree that the methods of making this type of bread are exceedingly uncertain; it is a prevalent opinion, too, that success is dependent very largely upon preparing a favorable medium and allowing the desirable organisms to get into it either from the air or utensils. Dr. Bailey and Margaret Mitchell state definitely that the leavening power is due to the presence of "wild" yeasts and that various bacteria contribute more or less to the odor and flavor of the bread; the bacterial fermentation, in the opinion of Dr. Bailey, is due to lactic and butyric ferments. Professor Harrison and Helen Atwater do not specify what the germs are that cause the spontaneous fermentation.

P. G. Heinemann and Mary Hefferan observed a bacillus which they were able to isolate but they do not say whether yeast was present or not. This bacillus, they maintain, is enabled by the use of milk to produce the acid necessary to liberate the carbon dioxide from the soda.

[1] *Science*, June 25, 1909, **29**, No. 756, p. 1011.
[2] *Bakers' Helper*, Nov., 1908, **22**, 1164.

"SAUERTEIG" METHOD.

There is another type of bread made by the use of the "Sauerteig," which, while it differs from salt-rising bread in many respects, has sufficient bearing upon the subject, as will be seen later, to warrant a brief review of some of the literature on the subject.

Long before the existence of microörganisms was discovered, it was known that when meal or flour and water were made into a paste it would, after a time, begin to ferment and evolve gas. This was early made use of in the preparation of bread and it was soon learned that a portion of the dough could be saved to start the fermentation in the next baking. This portion of dough would continue to ferment and become sour, hence its name "Sauerteig," but when mixed with fresh flour and water it would again become active and raise the bread. This method of making bread was, and in some countries is still, used very extensively, particularly in making whole meal bread ("Schwarzbrot") and rye bread. It is similar to the salt-rising method in that the fermentation in both is spontaneous; they differ, however, in that the former is started with hot water or milk, usually boiling, while the latter is made with tepid water. They differ also in that salt-rising bread is made from fresh meal each time while by the "Sauerteig" method a portion of fermented dough is saved for the next baking, and when a housewife or baker is out it is usually obtained from a neighbor. This method of making bread, while it is crude and uncertain compared with the methods of to-day which involve the use of compressed yeast, is, as would be expected, more certain than the salt-rising method because each time a portion of dough is saved for the next baking which insures the presence of the essential organisms although they may be badly contaminated with others.

A microscopic examination of a "Sauerteig" reveals both yeast cells and various bacteria in great numbers; at times the former and at times the latter exceed in numbers, and it has been the subject of many investigations to determine the rôle of each in the preparation of bread by this method.

The earliest view was that this bread was leavened by means of an alcoholic fermentation due to the presence of yeast.[1] This view was supported by various analyses that showed the presence of both sugars and saccharifying enzymes in flour, and later the alcohol in the fermented dough. Further, microscopic examination revealed the presence of yeast which was shown to have the cultural characteristics of *Saccharomyces minor* Engel.

In the year 1883 Chicandard[2] advanced a new theory, according to which the fermentation in this bread is due to a bacterium, which he claims produces gaseous products from the albuminous substances in flour.

In support of this theory he says that diastase does not saccharify starch at ordinary temperatures and that there is no decrease in the sugar content of dough during fermentation. As a matter of fact, however, sugar is a normal constituent of flours, and diastase has been shown to be active even at the temperatures at which doughs are ordinarily fermented.

Further, he maintains that there is no alcohol in dough which also has been proved to be contrary to fact. As a further support of his theory he gives an analysis of the evolving gases which consist of about 70 per cent. of carbon dioxide and the remainder of hydrogen and nitrogen. These gases are similar to those evolved from decaying albumin, which he gives as additional evidence in favor of his theory. Peters[3] thinks, however, that the carbon dioxide may have been produced by yeast, that the nitrogen may have come from enclosed air and the hydrogen may have been produced by a butyric ferment.

Laurent[4] found that an organism which he called *Bacillus panificans* is normally present in flours. This organism is killed only after heating to 100° C. for 10 minutes and is probably not killed in the baking of the bread. When growing in dough, it produces acetic, lactic and butyric acid, together with CO_2 but no hydrogen nor nitrogen. According to Laurent it is the cause of ropiness in bread, and in the opinion of Maurizio is identical with *Bacillus mesentericus vulgatus*.

An investigation by Dünnenberger[5] leads him to believe that the essential organism in the preparation of bread by this method is yeast and that the presence of bacteria is, at least, unnecessary if not even harmful.

In three papers on "Die Organismen des Sauerteigs und ihre Bedentung für die Brotgährung," Peters[6] reviews the literature on the subject and gives the results of his own exhaustive investigation. He finds numerous yeast cells and many bacteria as well, in a normal "Sauerteig." He succeeds in isolating *Saccharomyces minor*, which has been obtained by previous investigators, another yeast which resembles this species closely, *Mycoderma vini* (*Sacchar. mycoderma*) and *Saccharomyces cerevisiae*. In addition to these four species of yeast he isolated five different bacteria which he describes minutely. He concludes from the results of his investigation that the fermentation of bread by means of the "Sauerteig" is complex in its nature and that no single organism is responsible for all the changes that take place. The Saccharomyces are important in that they produce the alcoholic fermentation which aerates the bread and the bacteria render soluble a portion of the constituents of the flour and produce a certain percentage of acidity which checks various other bacteria that cause diseases in bread.

According to Lehmann's[1] investigation there is present in the "Sauerteig" together with numerous yeast cells a gas-forming bacterium. Upon a gelatin plate made from the dough numerous yeast colonies develop, which upon further examination agree in morphology and cultural characteristics with *Saccharomyces minor* Engel. Among the yeast colonies there usually appear comparatively few colonies of bacteria. If, however, an agar plate is made and incubated at about 37° C. the yeast colonies do not appear, but numerous colonies of bacteria develop, among which one form greatly predominates, others appearing far less plentifully and regularly. This predominating organism which he calls *Bacillus levans* grows on gelatine plates in white water colonies which are spherical in shape with a rather darker zone in the center. It is facultative anäerobe and grows in an atmosphere of CO_2. It is a gas former and now and then bubbles will appear even in sugar-free bouillon gelatine media. In the presence of sugar it produces gas in gelatine and agar media both on plates and in stab cultures. In bouillon media it produces cloudiness while if sugar is added gas is evolved. The organism is motile; does not form spores.

The gases that evolve from sugar bouillon, outside of a little nitrogen, consist of approximately $^1/_3$ hydrogen and $^2/_3$ carbon dioxide. Hydrocarbons were not detected. In sugar-free bouillon only very small quantities of hydrogen were produced and no carbon dioxide. A more complete analysis of the gases produced by this organism is given by Maurizio.[2] It was grown in sugar-bouillon and the results of the gas analysis follow:

	Beerwort. 1.	Diluted beerwort. 2.	Sugar-free bouillon. 3.
Carbon dioxide	68.9	66.8	63.7
Hydrogen	25.4	28.7	31.8
Nitrogen	5.7	4.5	5 5

The variation indicated by the figures above he attributes to the fact that carbon dioxide is absorbed to some extent by the medium.

When grown in different media the gases produced by this bacillus show considerable variation.

	Beerwort. 4.	Diluted beerwort. 5	Sugar-free bouillon. 6.
Carbon dioxide	68 4	63 8	0
Hydrogen	22.1	28.7	67.1
Nitrogen	9.2	7.5	32.9

[1] *Botanische Zeitung*, **47**, 404 (1889).
[2] *Ibid.*, **47**, 407 (1889).
[3] *Ibid.*, **47**, 408 (1889).
[4] "Getreide Mehl und Brot. Maurizio," p. 238
[5] *Botanische Zeitung*, **47**, 410 (1889); (*Botanische Centralblatt*, 1889).
[6] *Ibid.*, **47**, 405, 420 and 435 (1898).

Centralblatt für Bacteriologie, **1894**, p. 350.
[2] "Getreide Mehl und Brot. Maurizio," p. 235.

There were obtained from 600 cc. 1 per cent. sugar-bouillon 300 cc. of gas, while in sugar-free bouillon only 30 cc. of gas were obtained from the same amount of media.

The acids that this organism normally produces in media containing sugar are designated as acetic, lactic and oxalic.

Lehmann succeeded in setting up a gaseous fermentation in flour, which had been sterilized by submerging in ether for several days and regained from the ether by evaporation, by subsequent moistening with sterile water and inoculating with this *Bacillus levans*. The evolving gases were the same as those from sugar-bouillon fermented by this bacillus, and the odor the same as that of the "Sauerteig." A similar portion of the sterile flour inoculated from the "Sauerteig" fermented in apparently the same way but an analysis of the gases showed, however, that hydrogen was invariably absent, which would indicate that this is due to the presence of yeast and that the gas in the "Sauerteig" is not produced by *Bacillus levans*.

A control in which the sterile flour was inoculated with both *Bacillus levans* and yeast also failed to yield hydrogen in the evolving gases, which would perhaps indicate that the bacillus is not active in the presence of the yeast. Also when both organisms were inoculated into the media the maximum evolution of gas was obtained much sooner and with a smaller degree of acidity than when the fermentation was due to *Bacillus levans* alone.

Outside of the rôle that *Bacillus levans* plays in bread-making, whether it be desirable or not, it is of interest from another point of view. It was observed by Wolffin and Lehmann that it strikingly resembles *Bacillus coli commune* especially in its morphology. Also it was possible to set up the same gaseous fermentation in a paste made from sterile flour and water with *Bacillus coli commune*, as occurs when the same material is inoculated with *Bacillus evans*. Both ferment maltose, grape sugar and lactose. *Bacillus coli* differs, however, in that it coagulates milk and also in the composition of the gases it produces.

When bouillon with 1 per cent. of grape sugar added was fermented with *Bacillus levans* and *Bacillus coli commune* the following gases were obtained:

	Bacillus levans	*Bacillus coli commune*
Carbon dioxide	66.5	22.3
Hydrogen	28.6	75.6
Nitrogen	4.9	2.1

The gases collected from a paste of sterile flour and water exhibit no marked variation from the above table as may be seen from the following:

	Bacillus levans	*Bacillus coli commune*
Carbon dioxide	66.5	23.3
Hydrogen	27.7	74.0
Nitrogen	5.8	2.7

Lehmann questions whether these differences in the composition of the gases are sufficient to distinguish this bacillus from the coli group, particularly when the variability of these bacteria is taken into account. Members of this group have been known to lose their ability to coagulate milk, or to ferment sugar after having been grown on sugar-free media for some time. Maurizio also is of the opinion that *Bacillus levans* belongs to the coli group and he, too, concludes, as Peters, that it is the function of the yeast to produce the gas necessary to aerate the bread, and further that various lactic bacteria are desirable in that they check the action of objectional forms such as butyric bacteria and members of the coli group.

The disagreement in regard to the theories concerning the leavening agent in salt-rising bread and the necessary ingredients, the uncertainty of manufacture, and the lack of uniformity in the finished product lead the author to investigate the subject, in order to ascertain definitely, if possible, what the leavening agent really is: whether "wild" yeasts, as the majority of writers on the subject claim; or the interaction of lactic acid formed by bacterial fermentation, with soda as others claim; and then perhaps to obtain the desirable organism in pure culture and propagate it for the production of bread of uniform quality, thus substituting more scientific methods for making this type of bread.

OBSERVATIONS.

The first step in the investigation was to start the fermentation from cornmeal, as is regularly done, and then also to make the bread in order to be certain that the fermenting mass contained the essential organisms. The first experiences of the author in making this bread were in harmony with the references on the subject in regard to the uncertainty of the method, and even after the bread had been made successfully a number of times, failures were of frequent occurrence, although care was taken to control temperatures, proportions of ingredients, etc.

After having made the bread successfully a number of times, a microscopic examination of the "emptyings" prepared in the customary way was made. This was found to be literally teeming with bacteria while yeast cells were not to be found. Since this was contrary to what was found in the literature, the examination was repeated again and again; each time, however, bacteria were present in great numbers while yeast cells were invariably absent. This indicates that yeasts play no part in this bread, and the question arises as to how these bacteria function in the dough, whether by producing acid which liberates carbon dioxide from the soda or by decomposing some of the constituents of the flour into gaseous products. It was observed that if a portion of these "emptyings" was transferred to sterile milk by means of the platinum loop, gas began to be evolved after 8 or 10 hours, and that a curd which was broken and full of holes, due to gas bubbles, would form. It was possible to transfer these bacteria from tube to tube and each time the same gaseous fermentation would be set up, which would indicate that the evolving gas is produced by the bacteria from the milk itself, and it becomes of interest to determine the relationship of the bacteria present in the fermenting batter.

It is only in exceptional cases, if ever, that a sample of natural media contains but a single species of micro-organism when in a state of fermentation. Often the activity of two or more species in the same media produce changes which neither could do of itself. When several species are simultaneously engaged in the consumption of the same medium, their association is termed symbiosis; as an example of this we may refer to the kefir grains which contain at least one species of yeast and two speçies of lactic bacteria, the simultaneous growth of which produces from milk the beverage known as kefir. Another common association of microörganisms is styled metabiosis, in which one species by its activities renders the medium suitable for the growth and development of another. A good example of this is the formation of vinegar from cider, due to the presence of yeasts which form alcohol from the sugar, and acetic bacteria which, after the alcoholic fermentation has ceased, transform the alcohol into acetic acid. The "Sauerteig" is perhaps an example of both symbiosis and metabiosis, inasmuch as there is the simultaneous consumption of sugar by yeasts and lactic bacteria, which relationship is that of the former, and later the conversion of part of the alcohol formed by the yeast into acetic acid, which, as it occurs in the manufacture of vinegar, has already been referred to as an example of metabiosis.

The microscopic examinations having shown that active microörganisms in salt-rising bread are bacteria, it becomes a question whether or not a pure culture can be obtained from the "emptyings" with which alone the bread can be made, or whether the necessary gaseous products of fermentation owe their origin to the combined activity of several species growing side by side.

After transferring the bacteria from one milk tube to another for several times and incubating at 40° C., it was observed that there was exhibited no great variety of forms, indeed the cells were strikingly alike except for slight differences in the length of rods.

It was therefore assumed that the fermentation is due to a single species and plates were made to obtain it in pure culture. The first set of plates was made with an agar-bouillon media and incubated at 40° C. After about 15 hours a good growth had appeared and a number of milk tubes were inoculated from those colonies which seemed to show differences and incubate at 40° C. The next day all the tubes showed a growth, for a soft curd had formed in the milk, but none of them showed any signs of gas production while the one inoculated from the tube from which the plating was made was giving off gas. Since the first plating resulted in a failure, it was repeated. Again numerous colonies appeared in the usual time and this time a larger number of tubes were inoculated from them and incubated at 40° C. Again a curd formed in each of the tubes but there were no signs of gas. After making numerous plates with this agar bouillon medium and isolating many cultures without obtaining any that would produce gas it was thought that perhaps the medium was not favorable for the gas forming bacteria and that it either did not appear upon the plates at all or became attenuated during the planting and lost its ability to produce gas.

Since soda is commonly used in making the bread it was thought that an alkaline medium might be more suitable. Therefore a portion of nutrient agar medium with 1.0 per cent. added lactose was titrated with phenolphthalein to an alkalinity of 1 per cent. and another to an acidity of 1 per cent. With each of these plates were made, both directly from the "emptyings," and a tube that was the result of several transfers, and numerous tubes inoculated and incubated at the usual temperature of 40° C., but again all efforts to obtain a gas-forming culture were in vain.

An effort was made to make a medium as similar as possible to the original "emptyings" by adding a portion of cooked flour to the agar medium. This medium, however, was so opaque that it could not be used successfully and was abandoned. As milk is commonly used in making this bread, plates were made with a milk-agar medium and a number of milk tubes inoculated and incubated. Upon observing them the next day one of them showed the characteristic gaseous fermentation. From this tube another set of plates was made and several tubes inoculated. These again were giving off gas after incubating over night. Since milk-agar plates are always rather opaque it was thought advisable to plate this culture upon clear media so as to be more certain that it was pure. This was done but not a tube produced any gas after incubating. This then was either not a pure culture or it lost its ability to produce gas during the plating on clear media. Further attempts to obtain another gas-forming culture by plating with milk-agar failed utterly.

It was observed that when the predominating culture from the fermenting batter was isolated and grown in milk that after a curd had formed the milk began to be peptonized near the surface and after standing a few days a large part of the curd was peptonized. The same effect was observed when milk-agar tubes were inoculated with this culture, only the peptonization proceeded downward in the tube much slower. In milk-agar tubes, inoculated direct from the fermenting batter, the peptonization of the milk was also observed near the surface while farther down gas was formed which at times pushed part of the media together with the cotton plug out of the tube. This latter effect was observed in broth-agar tubes also when the media was boiled to expel air. Plates made from the organisms after having been grown under these anaerobic conditions yielded no culture that would produce gas.

When milk-agar plates are poured in Petri dishes about $^3/_4$ of an inch deep and 6 inches in diameter, the milk begins to peptonize from the top downward until after several days the medium loses its opaque character entirely and becomes yellowish in color. In these deep plates gas bubbles at times form near the bottom of the plates which may be due either

to a single organism or to several. To obtain cultures of these, the plate was inverted to allow the medium to drop out, when tubes could be inoculated by touching the gas bubble with a platinum loop. Milk tubes inoculated in this way showed the characteristic gaseous fermentation after incubating over night, but when plates were made from them and tubes inoculated from colonies, no gas appeared.

Single cells isolated from the fermenting batter by Dr. M. A. Barber's pipette method reacted in milk as those obtained by plating. A soft curd was first formed which later was peptonized from the top downward. When allowed to grow under a cover glass in an incubator at 40° C. a good growth was observed both in milk and broth. Spores formed readily. Single spores put into sterile milk and incubated produced the same reaction in milk as the cells themselves. No culture was obtained by this method that produced gas.

After all these failures to obtain a culture that was pure without a doubt and would retain its gas-producing power, it was thought that perhaps this gas formation was due to a mixture of cultures—perhaps a case of symbiosis or metabiosis. Upon this assumption plates were made and a number of tubes inoculated and incubated. After a good growth had set in, the tubes were numbered and fresh tubes inoculated from them by means of a platinum loop, mixing the various cultures. For example one tube was inoculated from Nos. 1 and 2, another from 1, 2 and 3, etc. The results of this mixing of cultures was as fruitless as all previous efforts, not a single tube showed any gas.

When sterile milk is inoculated from the fermenting batter, gas is driven off after incubating 6 to 10 hours and a curd is formed which is carried to the top by the gas bubbles and then assumes a tough leathery character. If after incubating for three or four days, sometimes less, a transfer to sterile milk is made, no gas appears. The same loss of gas production occurs in three or four bays if transfers are made at intervals of either 12 or 24 hours. A falling off of gas production is also observed in the fermenting batter; after gas bubbles begin to form the rate of gas production increases for about three or four hours and then gradually decreases. After fermenting for 8 to 10 hours, it becomes very much weaker and does not regain its strength if used in making the sponge and dough. In the latter the weakness is even more apparent than in the former, and when once the batter has fermented too long, the loaves are apt to be only about one-half the normal size. This gradual weakening of the batter has been observed by bakers, as well, and is popularly termed "working itself out." They also observed that when once it has become weakened and lost its gas-producing power that it will not regain its strength by the addition of fresh food material as is done in making the sponge and dough. While it was not possible to propagate the bacteria in liquid media from time to time to be used in making bread, a dried product was prepared which could be used at will with good results.

The product was used by the author in making salt-rising bread in numerous experiments and was also given out to a number of housewives who used it successfully. That the artificial cultivation of bacteria can be of value to the manufacturing baker as well was demonstrated by giving this product a thorough trial in a modern baking plant where the bread was not uniform and it was necessary at times to add compressed yeast to insure proper aeration. From 800 to 1000 loaves were made daily for a month and the bread was uniform in quality and was ready for the bench at the desired time every day while formerly it was often ready sooner or later than desired and consequently upset the system of the plant. The batter made from the product begins to ferment not only more regularly but sooner than if made with meal. One pound is sufficient for the production of 400 to 500 loaves of bread.

The fact that the fermenting "emptyings" made from this product reveal cells which are strikingly alike, a large sporebearing motile rod greatly predominating, and that once a gas-forming organism was obtained by plating, and this one lost its ability to produce gas after incubating several days, indicates that the gas formation owes its origin to a single organism, which becomes attenuated during the plating. This is corroborated by the fact that a falling off of gas formation is observed both in the batter and when transfers are made to sterile milk, and is further supported by the fact that from either broth or milk-agar plates, in which the colonies were extremely thick, portions of media so large that all organisms should be included could be transferred to sterile milk and no gas would be evolved, which seems clearly to indicate attenuation.

Another instance in which the loss of gas production was observed may be referred to here. In a modern bakery bread is mixed with huge mixers in lots of about 800 to 1500 pounds of dough. A certain make of these mixers is run at very high speed making about 160 revolutions per minute, which is several times that of the average mixer. This extreme treatment is considered very desirable in making ordinary bread as it develops the elasticity of the gluten and improves the color of the bread. A batch of salt-rising bread was tried in one of these mixers, taking out a portion of dough after mixing 6, 15 and 30 minutes, respectively. The loaves made from the dough that was mixed 6 minutes rose very slowly, and were poor in quality, while the loaves from the portions of dough that were mixed 15 to 30 minutes, respectively, failed utterly to rise, even after standing several hours, while when mixed in a slow-speed mixer they rise in 30 to 45 minutes.

Such variation is not without parallel as may be seen from observations made by Klein,[1] on *Bacillus enteriditis sporogenes*. If deep liquid sugar-gelatine tubes (8 cm.) are inoculated with the bacilli or spores

[1] *Centralblatt für Bakteriologie*, **18**, I Abteilung, No. 24, p. 737 (1895).

of this organism and incubated at 20° C., the medium is liquefied after 48 hours, with the formation of very few indeed, if any, gas bubbles and the organism sporulates freely. If, on the other hand, a stab culture is made from the same culture into a similar medium, gas formation begins within 24 hours and the medium is torn and rent by the evolving bubbles. In such a culture in which gas is abundantly given off, complete liquefaction takes 8, 14, or even 20 days, instead of 48 hours, and spore formation is not observed. The gas is principally methane.

A violent evolution of gas, after incubating from 1 to 2 days which breaks the layer of cream, accompanied with the formation of a curd which separates from the clear acid whey, is given by Klein[1] as the typical characteristic of this organism in milk.

If two gelatin tubes are inoculated with spores and the bacilli of the organisms, respectively, and incubated for several days, the results are so different that it is difficult to believe that the two cultures are identical, for the former shows the typical spherical liquefying colonies, while in the latter only small non-liquefying spots appear.

By transferring spores of the organism to fresh sugar-gelatine for a number of times, it undergoes marked changes in its cultural characteristics. It soon acquires greater liquefying powers, a tendency to form threads and the ability to rapidly form spores. In milk these variations are quite pronounced, for it no longer produces the changes which have been described as typical. Instead of the violent evolution of gas which disturbs the layer of cream, the formation of a curd and the separation of a clear whey, the milk undergoes an entirely different transformation, in which there is no gas whatever evolved and the cream is not disturbed. After several days the milk immediately underneath the cream begins to be decomposed into a yellowish solution which remains separate from the white coagulum underneath. The whey in the typical milk culture smells of butyric acid and reacts acid while the yellow solution of the atypical culture is weakly alkaline and has a foul odor. The bacilli in the typical milk culture are short rods without spores, while those of the atypical culture often appear in threads which as well as the short rods sporulate within a few days. When once the organism has changed so that spores when repeatedly transferred to milk continue to give the atypical culture characteristic, the change is permanent and it does not revert to the original form. The virulence in the atypical is almost or entirely lost.

On the suggestion of Professor Stephens some "emptyings" were obtained from a lady who makes salt-rising bread which he at one time found to be teeming with both yeast cells and bacteria. This was contrary to what had been observed, but as it agreed with a number of the references a microscopic examination was made, but again many bacteria were present and no yeast cells. From these "emptyings" a set of plates was made and a number of tubes inoculated. On removing them from the incubator the next day several of them were evolving gas. One of these cultures was plated repeatedly on both milk and broth-agar media and each time all the colonies appeared alike and all the tubes inoculated were evolving gas after standing in the incubator for about 15 hours, which is sufficient evidence that it is a pure culture, and it becomes a question as to whether it is capable by itself to properly ferment bread. The mere fact that it will produce gas when growing in milk is not sufficient evidence that bread can be made with it, for often the "emptyings" will apparently be fermenting normally, but when made into a sponge by the addition of water and flour the production of gas almost ceases, and when the dough is made it fails utterly to rise. Indeed at times both the "emptyings" and sponge will appear normal and the dough will fail to rise, and it has happened in practice that a batch of about 1000 pounds of dough was run through the mixer, divider and moulder, and after being put into pans failed to rise and had to be taken from the pans and mixed with compressed yeast.

In order to determine whether this bacterium is of itself capable of aerating bread, it is of course desirable to use sterile flour; this unfortunately can be obtained only with difficulty and perhaps not at all without altering the character of the flour and destroying to a certain extent its bread-making qualities.

One of the two methods that have been employed is by heating the flour to a temperature of 115° to 120° C. This temperature is not sufficiently high to completely sterilize the flour for spore-forming organisms certainly survive, and besides it darkens the flour and, according to Peters, destroys its ability to form a dough. The other method of submerging the flour under ether for several days is more satisfactory, as it is less injurious to the flour, but it is a difficult matter to sterilize enough to be used in baking tests.

In these experiments it was thought best not to sterilize the flour but to grow the bacteria in sterile media up to the time the sponge was made, which would give the bacteria in the flour only from two to four hours to become active, for it was never more than four hours from the time the sponge was made until the bread was put into the oven and usually between two and three hours. When a dough was made without the addition of either bacteria or yeast, no marked changes were apparent within three or four hours, and if yeast was then worked into it, it would begin to rise and after fermenting properly, nearly normal bread could be made, which would indicate that the bacteria in flour do not have a marked effect upon a dough within three or four hours.

As already stated, milk is a common ingredient in salt-rising bread, and as it can be sterilized conveniently, it was used in the following baking experiments. With this pure culture bread was made from the following ingredients: 800 grams of flour, 100 cc. sterile milk, 410 cc. water, 12 grams salt and 15 grams sugar. The sterile milk was inoculated with the pure culture obtained and incubated 17 hours, when it was made into a sponge with 175 grams of flour and 200 cc. water. After the sponge

[1] *Centralblatt für Bakteriologie*, **22**, I Abteilung, p. 577.

began to drop, which took about two hours, the dough was made by mixing the sponge with the remainder of the ingredients and moulded into loaves and put into pans at once. The bread rose well and was baked in the usual way and had the characteristic odor and taste of salt-rising bread. This experiment was repeated a number of times, which indicates that this bacterium is able by itself to properly aerate bread. Bread was also made by the "straight dough" process in which all the ingredients are mixed at once leaving out the sponge stage. In this experiment the whole of the liquid used was milk fermented by this bacterium, which was made into a dough by mixing with the other ingredients. The dough was at once moulded into loaves and put into pans. It rose rather slower, than when a sponge was made, and produced bread of poorer quality. "Straight dough" bread was also made by using as the liquid $^1/_2$ fermented milk and $^1/_2$ water; also by allowing the bread to rise, as is always done in making yeast bread, previous to moulding into loaves. This bread rose faster in the pans and the loaves had more of a tendency to crack. The bread was coarser in texture and when cut crumbled easily.

This bacterium could be propagated by transferring to fresh milk occasionally. After standing two months, however, it had become much weaker, and while it would still produce gas when grown in milk, it would no longer raise bread. Even by transferring to fresh milk a number of times it failed to regain its strength. After 200 cc. of milk fermented with this organism had been kept for 9 months in a German flask closed with a cotton plug, it was impossible to abtain any growth whatever by inoculating sterile milk from it.

An effort was made to prepare a dry product containing this organism to be used in making bread. This was done by growing the pure culture in sterile milk and then mixing flour to make a sponge. After the sponge had risen and fallen it was spread on panes of glass in thin layers and allowed to dry. Some of this dried product was mixed with meal and was used in starting the bread in the usual way. When the liquid used in starting the "emptyings" was heated to the boiling point the addition of some of this dried material seemed to make no appreciable difference either in the regularity or the time it would take to show the formation of gas bubbles, as was observed by setting at different times, a number of emptyings in Erlenmeyer flasks plugged with cotton, both with and without any added material. When the meal was stirred into the boiling milk a temperature of 85° to 90° C. was obtained. When the milk was heated to 90° C., it seemed rather doubtful whether the addition of some of this product was noticeable; if heated to 80° or 70°, however, it was observed that gas began to form both sooner and more regularly if a portion of the dried product was added, which would indicate the possibility of preserving this organism in the dry state for its economic use.

The source of the organisms involved, especially when the bread is made without adding them by artificial means, is one of the important considerations in making this kind of bread. It is the opinion of Dr. Bailey, Professor Harrison and Margaret Mitchell that they get into the prepared medium either from the air or utensils and that failures are far less frequent in places where the bread has been made for some time. To determine whether or not the desired bacteria get into the medium from the air, a number of Erlenmeyer flasks were partially filled with the usual ingredients in the proportions that they are used in the "emptyings." These flasks were plugged with cotton and sterilized by steaming for about 45 minutes on three or four consecutive days. After incubating for a few days to make certain that all life in the flasks was destroyed, the plugs were pulled and the flasks set in a gas oven which had been repeatedly used as a place to keep the "emptyings" and sponges as well while they were fermenting. If these bacteria are propagated from one baking to another by means of the air then this oven should prove a particularly fertile source, and as the media was properly prepared and the temperature carefully regulated, these flasks should soon show the characteristic fermentation. As a matter of fact, however, it was only occasionally that a gaseous fermentation would develop in these flasks and then with great irregularity; the gas bubbles would first appear near the top of the media and later they would form farther down and never did they occur uniformly throughout the media as is the case when the "emptyings" are set in the usual way. Often an abnormal fermentation would occur in these flasks; at times this would become manifest in a souring of the media without any gas formation, and at other times various moulds would appear on the surface of the media. This would indicate that the air is not the true source of the gas-forming organism, and although it may get into the media from the air at times it cannot be relied upon to produce the desired fermentation with any certainty or regularity.

In how much the utensils serve as a means of propagating the bacteria evidently depends to some extent upon the operator; if they are thoroughly cleaned each time after use, the chances are that the bacteria are nearly all removed with the ingredients; on the other hand if carelessly cleaned, it is possible that enough bacteria will be retained to again start the fermentation. At best, however, this cannot be a reliable source, and as the bacteria would be only on the sides of the vessel, some time would elapse before they would get into the center of a non-liquid medium. It is the experience of the author that it matters little, if any, whether the "emptyings" were made in vessels that had been previously used or not.

Evidently the milk is not the source of the organisms for the bread can be made with water, also it is possible to obtain the gaseous fermentation by inoculating sterile milk with cornmeal. The true source seems to be the cornmeal, and it is the experience of bakers and housewives that the more highly cleaned meals do not give as good results, which would indicate that it is associated in some way with the exterior of the grain of corn. It is the experience

of housewives, and canning factories as well, that it is a difficult matter to can corn so that it will keep; often the ends of the cans bulge out, owing to the formation of gas which may be due to the survival of the salt-rising organisms.

As already stated, it has been a matter of much dispute as to what ingredients are necessary in making salt-rising bread, and something over two hundred baking experiments were made to determine the necessary ingredients, the proportions in which they would be used, the most favorable temperature, etc. These baking experiments were taken up as systematically as possible, observing the effect of changing one thing at a time both upon the rate of the evolution of the gas and the character of the bread produced, and keeping a careful tabulated record of the results, some of which will be given here. One series of these experiments was made to determine the effect of milk, and the following table shows the proportions of the ingredients used, when they were mixed in "emptyings," sponge and dough, and the temperature of each (see Table I). The ingredients in Nos. 101, 102 and 103 are precisely the same in quantity, differing only in that No. 101 had the milk added in the "emptying," No. 102 in the sponge and 103 in the dough. It is evident from the table that the emptyings in 101 were light and ready to be made into the sponge by 8:50, while 102 and 103 required 40 minutes longer; in the sponge it was observed that 101 was more active than 102 and 103 still more sluggish. In the dough the advantages of adding the milk in the early stages were still more apparent. The bread from 101 was largest in volume and best in every way, No. 102 was rather heavy and 103 failed to rise more than about one-half the usual height. From these experiments it is evident that milk has a marked influence upon the growth of the bacteria and consequently upon the character of the bread produced. Various baking experiments were made to determine to which of the constituents of the milk to attribute this.

It was found that whole milk did not give appreciably better results than skimmed, which would indicate that the butter fat, while certainly it has a "shortening" effect, as all fats do, has no bearing upon the gas production of the organism. The other two important constituents of milk, namely the casein and milk sugar, were used separately in making the bread. Four different samples of casein were obtained: two made from the buttermilk and two from skim milk.

It was found that when the "emptyings" were set as in No. 101 with 10 grams of casein instead of 10 grams of powdered skim-milk, gas began to form several hours sooner, especially when the buttermilk caseins were used, as may be seeen from bakings 132 and 134. Even five grams of casein which is about the equivalent of casein in 10 grams of powdered skimmed milk was more effective than the latter and almost as effective as 10 grams of the same material. In baking Nos. 133, 134, 135, all of which were made with casein, the gas began to be evolved about $2^1/_2$ hours sooner than in No. 132 which was made with powdered skimmed milk. No. 134 showed signs of gas about $^1/_2$ hour sooner than 133 and 135 but it was made into a sponge about the same time.

When lactose was used instead of milk in the above formula the gas began to form little sooner than if it was not used. Both lactose and casein used together were apparently no more effective than the same amount of casein alone. These experiments would indicate that the essential constituent of the milk is the casein rather than the milk sugar or butterfat.

	1909.									1910
Batter.	Date	11/3	11/3	11/3	11/14	11/14	11/14	11/14	11/10	11/10	5/9
	No.	101	102	103	132	133	134	135	112	115	378
	H_2O	150	150	150	150	150	150	150	150	150	150
	Dried milk	10	10	10	10	5A[1]	10A[1]	5B[2]	10M[3]	3C[4]	5
	Cornmeal	20	20	20	20	20	20	20	20	20	22
	Sugar	4	4	4	0	0	0	0	0	0	...
	Starter	2	2	2	2	2	2	2	2	2	2
	Soda	2½	2½	2½	2½	2½	2½	2½	2½	2½	2
	Time	9.30	9.30	9.30	10.30	10.30	10.30	10.30	10.30	10.30	8.30
Sponge.	H_2O	200	200	200	200	200	200	200	200	200	200
	Dried milk	0	10	0	0	0	0	0	0	0	0
	Flour	150	150	150	150	150	150	150	150	...	150
	$NaHCO_3$	0	0	0	0	0	0	0	0	...	...
	Time	8.50	9.30	9.30	12.05	9.30	9.30	9.30	8.30	...	2.20
	Temp.	40	41	41	43	42	40	40	40	...	41
Dough.	H_2O	200	200	200	200	200	200	200	200	...	200
	Flour	650	650	650	650	650	650	650	650	...	650
	Sugar	0	0	0	0	0	0	0	0	...	0
	Salt	12	12	12	12	12	12	12	12	...	12
	Oil	0	0	0	0	0	0	0	12	...	0
	Time	10.00	11.00	11.40	1.05	10.50	10.45	10.35	9.55	...	3.30
	Temp.	37	37	37	38	39	38	38	39	...	41
	Oven	11.00	12.10	...	2.00	10.15	12.00	12.00	11.05	...	4.25
	Out	11.45	...	...	...	...	...	...	11.35	...	...

[1] A in 133 and 134 is casein from skim-milk.

[2] B in 135 is casein from another sample of skim-milk casein.

[3] M in 112 is malt extract.

[4] C in 115 is asparagin.

Note: All batters, except in No. 378, were set in the evening at the time given and the sponges in the morning of the next day. No. 378 was finished in one day.

The two samples of buttermilk casein, as stated above, favored the gas production more than those made from skim-milk and also more than the powdered milk itself. This may perhaps be partly explained by the fact that the casein from buttermilk undergoes a partial hydrolysis during the fermentative process of buttermaking, which may render it more assimilable by the bacteria. Also it was observed later that $2^1/_2$ grams of soda in the above formula made the media rather alkaline and checked the fermentation somewhat, and as the caseins, especially those made from buttermilk, reacted acid, neutralized a part of this alkali and made the medium more favorable to the growth of the baeteria.

Malt extract which is used extensively in making ordinary bread also proved to be of value in making salt-rising. By the use of 10 grams of malt extract as in baking No. 112 it was possible to make good salt-rising bread. The value of malt extract is perhaps to be attributed both to its content of maltose and various soluble nitrogenous substances, and it is a question whether the enzymes have the same value that they do in making bread with yeast, especially those that have a proteolytic action, for the bacteria themselves have a marked action upon the gluten.

The addition of three grams of asparagin, as in No. 115, was detrimental and there was no gas production even after standing for several days. Ammonium nitrate was added to the formula in quantities varying from $^1/_2$ to 5 grams, and it was found to retard the production of gas in all cases and when more than about 2 grams were used, gas failed to be produced at all. Potatoes and ginger, which are at times used, were tried but no beneficial effects were observed.

A series of "emptyings" were set in the same way using different sugars, *i. e.*, maltose, cane sugar, dextrose and lactose, and it was found that the gas began to evolve sooner than if no sugar was added to the meal. These sugars, as near as could be observed from the time bubbles began to form, were all fermented equally well and also as far as the production of bread is concerned.

These results were confirmed by adding 1 per cent. of cane sugar, maltose lactose, dextrose and dextrin respectively to separate portions of a nutrient agar medium and inoculating with a small loop full direct from the fermenting batter. The agar medium to which the carbohydrates, named above, were added contained 10 grams peptone and 5 grams beef extract to a liter of water. Seven hours after inoculating the tubes containing carbohydrates were all rent with gas bubbles and the medium in each tube was raised to about twice the initial volume. The tube containing no sugar showed only a few small bubbles which did not increase appreciably with longer incubation, while in a control no gas bubbles were observed. The dextrin and sugars were all fermented equally well.

The addition of milk accelerates both the production of gases and acids. It was repeatedly observed that those "emptyings" which were set with milk or casein began to throw off gas sooner and more rapidly and, too, that the evolution of gas ceased sooner and the medium became sour. For example on one occasion the "emptyings" made without milk were allowed to stand at a temperature of 40° C. for 31 hours or 25 hours after gas bubbles appeared and it was still alkaline and gas was given off, while when milk is added it becomes sour in a very much shorter time and the evolution of gas ceases. This has been observed by bakers as well, and the author has been told that the addition of milk causes the fermenting material to "work itself out" much sooner. When once the evolution of gas has ceased the "emptyings" no longer work well, if at all, when used in making the sponge. This is quite different in fermenting either a batter or a clear wort with yeast, for after the fermentation has ceased and the yeast settled to the bottom, it can be saved for a week or more and used in making a sponge. This also accounts for the fact that a portion of salt-rising dough cannot be saved for the next baking with the same success as can a portion of dough made with "Sauerteig," for the ferments in the former rapidly lose their gas-producing power and fail to regain it with the addition of fresh flour and water. The "emptyings" as well fall off in gas production after fermenting for some time. After the first bubbles appear, the rate of evolution of gas increases to a maximum and then gradually decreases. When once this maximum has been passed they no longer give good results when used to make bread, for the weakening in gas production becomes even more pronounced in sponge and dough.

It is well known that, in all fermentative processes, the temperature is of great importance, and in a modern baking plant the temperature of the dough is under almost perfect control, varying only a degree or two from day to day during the four seasons of the year. Bakers who make salt-rising bread have found that 26.6° (80° F.), the temperature at which ordinary bread is fermented, is far too low for this type of bread. To determine at what temperature the salt-rising organism is most active a number of "emptyings" were made in the usual way and placed in ovens at a temperature of 35° C., 40° C., 45° C., 50° C., 55° C. and 60° C., respectively. It was found that the optimum temperature lies somewhere between 40° and 50° and that it is possible to ferment bread of about equal quality anywhere between these two temperatures. At 35° the gas is evolved very much slower and when the bread is put into pans it takes considerably longer for it to rise to the usual height. When set at 55° C. the gas is formed slower than at lower temperatures while at 60° C. only a few bubbles of gas are formed in 24 hours. From these results it is apparent that the bacteria grow and can be used in making bread through as wide a range of temperature as yeast although it is about 15° C. higher.

It is the experience of the author that best results are obtained by fermenting the "emptyings" and sponge at a temperature rather lower than the optimum and then taking the water used in making the dough hot

enough to bring it to a temperature of 42° to 46° C. In bread made with yeast as well it is in accordance with the best bakery practice to increase the temperature toward the latter stages of the fermentation.

Sudden changes of temperature seem to have no marked influence upon the bacteria other than accelerating or retarding the rate of fermentation, for good bread was made from "emptyings" that had cooled to 22°, by making the sponge in the usual way at 39° C. and the dough at 42° C. This is of practical importance, for often in practice the "emptyings" are not kept at constant temperature. In the later stages, however, especially in the dough, it is essential that the temperature should be up to 40° C. or over.

[*To be continued in February.*]

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A RAPID METHOD FOR THE DETERMINATION OF SULPHUR IN ROASTED BLENDE.

By C. C. NITCHIE.

Received November 10, 1911.

As usually conducted, the sampling and analysis of the roasted ore drawn from a blende roasting kiln furnishes information useful only for purposes of record. A small portion is taken from each car load drawn and all such portions are mixed at the end of a day to make an average sample, which is analyzed on the following day.

This practice gives only average results, is of no value in determining the quality of ore from the individual draws, and fails entirely to detect the occasional car of poorly roasted ore which is transferred to the storage bins. It relies only on the judgment of the kiln men to determine when the ore is sufficiently roasted to be suitable for use in the spelter furnaces, and when it should be returned to the kiln for additional roasting.

In order to put the disposition of the ore on a definite basis, each draw should be sampled and analyzed for sulphur immediately after leaving the kiln. No ore should be placed in storage until the analysis is reported, showing that the sulphur is below a previously fixed maximum.

The usual gravimetric method of sulphur determination is unsuitable for such control analyses, on account of the time required, which would necessitate holding the ore in the car for a considerable length of time.

About a year ago Mr. M. F. Chase suggested to the writer that a rapid method, suitable for such determinations, might be devised by heating the ore sample in a current of air, absorbing the resulting oxides of sulphur in an excess of a standard alkali solution and titrating the excess. Based on this suggestion, the method to be described was worked up and has been in regular use since January, 1911.

In the kiln, the constituents of the original ore are mainly converted into oxides. Some remain partly in the original sulphide condition, while a small part of the zinc, some of the lead, and all of the lime are present as sulphates. On heating this ore in a current of air to a bright red, all of the sulphides are oxidized, giving the corresponding metallic oxides and sulphur dioxide with a little sulphur trioxide. The sulphates of zinc and lead are decomposed, giving zinc and lead oxides and sulphur trioxide. The calcium sulphate, however, is not easily decomposed by heat and remains unchanged, unless the temperature is raised to a point much higher than would be practicable in any roasting furnace. Strontium and barium would probably be present as sulphates. This has not been confirmed as none of the ores on which the method has been used have contained these elements.

At first thought, this property of the calcium sulphate might seem to be a drawback to the method, but, as the result wanted is an index of the completeness of the roast, and as, even under the best conditions at the kiln the calcium in the ore will always retain its equivalent in sulphur, no real error is introduced. The result obtained is the so-called "false sulphur," the sulphur which, under proper conditions, might have been removed from the ore in the kiln.

An unforeseen phenomenon is the evolution of copious fumes of zinc oxide as long as any sulphide remains unoxidized. This undoubtedly comes from the reduction of the zinc oxide and sulphate by the zinc sulphide (reactions analogous to the well known reactions in the smelting of lead sulphide ores) with volatilization of the zinc and subsequent oxidation by the air current.

$$2ZnO + ZnS = 3Zn + SO_2$$
$$ZnSO_4 + ZnS = 2Zn + 2SO_2$$
$$2Zn + O_2 = 2ZnO$$

The cessation of this evolution of zinc oxide furnishes a very accurate indication of the completion of the decomposition of the sulphides and sulphates of the ore, and of the absorption of the sulphur oxides.

The fume is not appreciably dissolved by the alkali solution. Numerous tests after absorption have shown, at most, faint traces of zinc, not enough to affect the determination. To prove that it is zinc oxide, it was collected over distilled water in an inverted bottle which was then covered and allowed to stand until the fume had settled. It was then dissolved in a little dilute hydrochloric acid and potassium ferrocyanide solution added. This gave the white zinc ferrocyanide precipitate.

Phenolphthalein is used as the indicator in the titrations, as it is equally sensitive to sulphurous and sulphuric acid, showing neutrality with the normal salts of both.

For heating the ore sample to drive off the sulphur, nothing can be superior to the electric tube furnace, on account of its simple manipulation, accuracy of temperature control and cleanliness. The furnace which has been in use here is one similar to that described by Mr. G. M. Berry,[1] with a fused silica combustion tube. It has given even better service than was claimed by Mr. Berry, as the original winding was in service over 4,000 hours at 1000° C.,

[1] THIS JOURNAL, **2**, 255.

part of that time for about twelve hours a day, and for nearly four months continuously without a shut down.

The ends of the tube are cooled by wrapping with strips of cotton gauze which dip into distilled water.

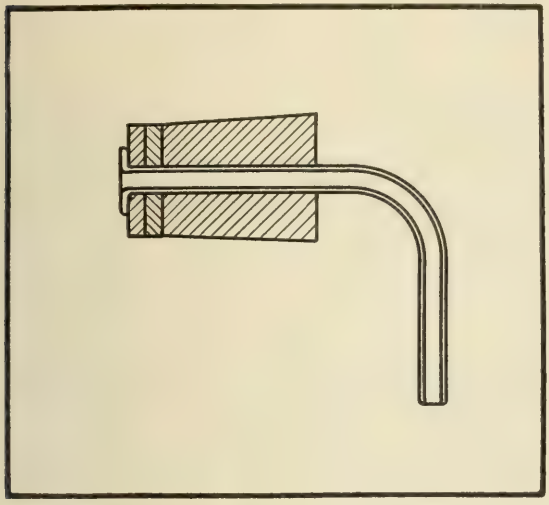

Fig. 1.

Tap water should not be used as it soon forms a crust of salts over the gauze, decreasing the cooling effect. An excellent reservoir for the cooling water consists of a rectangular box of galvanized sheet iron of about the same length as the combustion tube, about six inches high and two inches wide. This is tightly closed except for two small openings, which communicate with laterally projecting troughs at the bottom near each end. This reservoir is filled with water and placed back of the furnace, with the small troughs under the ends of the combustion tube to receive the free ends of the gauze. Atmospheric pressure keeps the water from flowing into the troughs except when evaporation has lowered the water level to the top of the openings. This reservoir contains enough water to last a week or two. Even where the ends of the tube are water-cooled, there is danger that the rubber stoppers may be overheated by the radiant heat. To avoid this the ends of the stoppers are protected by discs of $^1/_8$" asbestos board of the same diameter as the tube, held in place by bordering the ends of the small glass tubes as shown in Fig. 1.

A convenient device for introducing the boat without the necessity of looking into the tube to make sure that the boat is not overturned is shown in Fig. 2. It is made of a piece of heavy wire, preferably of nickel or some other metal not easily corroded or rusted. One end is flattened out and so bent that the end projects over the end of the boat and in contact with it when both boat and wire are resting on the bottom of the combustion tube. The other end of the wire is bent at a right angle to make a hook for withdrawing the boat and also to indicate when the rod is in the proper position to keep the boat upright. A notch is filed around the wire or a finer wire wrapped around it as a guide at the point which is flush with the end of the tube when the boat has been pushed to the middle of the tube.

The solutions needed are an accurately standardized solution of sulphuric acid and one of equivalent strength of sodium hydroxide. A convenient solution is equivalent to 5 milligrams sulphur per cc. One cc. will then equal 0.5% sulphur on a 1-gram sample. The two solutions should be as nearly equal as possible to avoid the necessity for corrections in reading one in terms of the other. There should be provided a reservoir of distilled water on an elevated shelf, with a siphon tube for use in diluting the contents of the absorption bulb to the proper volume, and for washing it out after the absorption.

The most convenient form of absorption vessel which we have found is the Murray potash bulb.

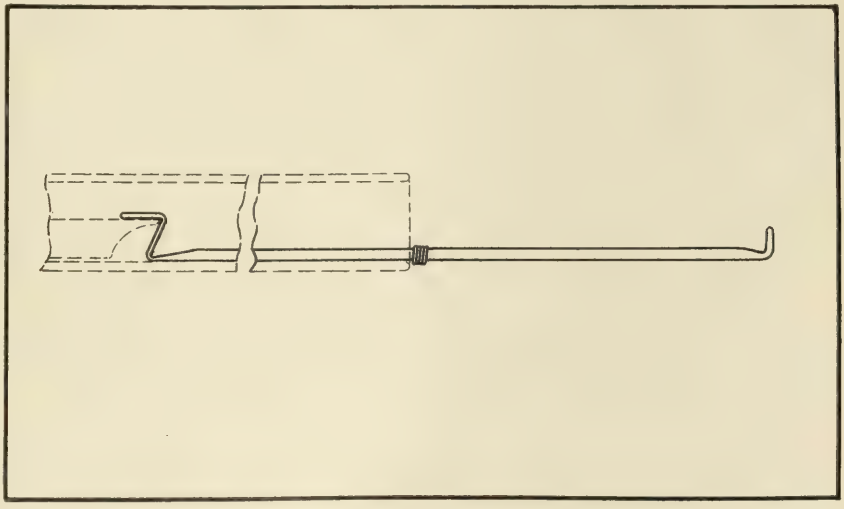

Fig. 2.

The method as in use at present is as follows:

Each car, as it is brought from the kiln, is sampled in two places by a spear sampler. This sample is cut down with a riffle to about 50 grams and ground with a few turns of the muller in a Buck's mortar.

Fine grinding is undesirable as it prolongs the time necessary for the analysis by restricting the free circulation of air through the ore. All that is necessary is to grind fine enough so that a one-gram sample will be fairly representative.

A measured quantity of the standard alkali solution is run into the absorption bulb. Seven to 10 cc. will suffice in practically all cases. This is diluted with distilled water to a volume that will bring the solution into the fifth bulb when the air current is passing. The bulb is then attached by a bent glass tube to the exit end of the furnace.

One gram of the ore is placed in a combustion boat and introduced into the tube of the furnace which has already been heated to about 1000° C. A moderately rapid current of air, freed from carbon dioxide by caustic potash or soda lime, is passed through the apparatus until the sulphur is completely driven over into the alkali solution. This usually takes about six minutes. When the zinc oxide fume has completely disappeared from the large bulb of the absorption vessel, the air current is stopped. The absorption bulb is disconnected and the solution transferred to a beaker, the bulb being thoroughly rinsed out with distilled water. A few drops of phenolphthalein are added and the standard acid is run in until the solution is colorless. If the acid and alkali solutions are exactly equivalent, the volume of acid required is subtracted from the volume of alkali originally taken for the absorption. The difference is the volume of acid equivalent to the sulphur which has been burned out of the ore. If the solutions are of the concentration mentioned above, this volume is divided by 2 to give the per cent. of false sulphur in the ore.

When the acid and alkali solutions are not exactly equivalent, the value of 1 cc. of the alkali in terms of the acid solution must be determined. The volume of alkali taken for absorption is multiplied by this factor, giving the equivalent volume of the acid solution. The volume of acid used in the titration is then subtracted from this equivalent volume and the result divided by 2 to give the per cent. of false sulphur.

If total sulphur is wanted, it is only necessary to add to the false sulphur $^{32}/_{56}$ of the per cent. of lime. With most ores the lime varies within comparatively narrow limits. It is usually sufficient for technical purposes to calculate, for a given grade of ore, the correction corresponding to the average per cent. of lime in that grade, and to add this correction to all determinations.

This method has been carefully checked up by running daily samples, both by the new method and by the gravimetric method. The accompanying table shows the results for twenty consecutive days on Wisconsin magnetic separator concentrates.

As a further check on the method, a number of ores were analyzed for (1) total sulphur by the gravimetric method, (2) lime, (3) false sulphur by the new method, and (4) fixed sulphur remaining in the ore after the volatilization of the false sulphur. The results are given in the following table:

False sulphur determined by new method. Per cent.	CaO.	CaO × 32/56.	Total sulphur (calculated).	Total sulphur (gravimetric).
0.6	3.4	1.9	2.5	2.8
1.1	3.0	1.7	2.8	2.8
1.1	3.1	1.8	2.9	2.9
1.2	3.0	1.7	2.9	2.9
0.9	3.3	1.9	2.8	2.8
0.9	3.5	2.0	2.9	3.0
1.2	3.1	1.8	3.0	2.8
1.2	3.0	1.7	2.9	3.1
1.0	3.0	1.7	2.7	2.7
0.9	2.8	1.6	2.5	2.6
1.0	2.8	1.6	2.6	2.9
1.0	3.0	1.7	2.7	2.7
1.1	3.0	1.7	2.8	2.8
1.0	2.8	1.6	2.6	2.8
1.1	2.8	1.6	2.7	2.9
0.9	2.4	1.4	2.3	2.5
1.2	2.8	1.6	2.8	2.5
1.5	2.5	1.4	2.9	3.0
0.9	3.0	1.7	2.6	2.6
0.9	3.1	1.8	2.7	2.8
		Average,	2.73	2.80

Total S (gravimetric).	CaO.	CaO × 32/56.	Fixed S (gravimetric).	False S (new method).	Total S (sum of false and fixed sulphur).
2.3	3.0	1.7	1.6	0.7	2.3
2.3	3.0	1.7	1.8	0.6	2.4
5.9	0.9	0.5	0.5	5.5	6.0
2.5	0.6	0.3	0.4	2.2	2.6

These figures show that, under the prescribed conditions, the fixed sulphur calculated from the per cent. of lime is the same as that found by analysis, and that the total sulphur calculated from the false and fixed sulphur is the same as that determined by analysis.

Attempts to use the method for the determination of sulphur in raw ores have led to low results, either from failure to absorb the larger quantities of sulphur gases or from condensation of part of the sulphur trioxide in the cooled portions of the tube. As there is not the same demand for a rapid method in the case of raw ores as in that of the roasted, these attempts have not been continued.

There is every reason to believe that a similar method could be applied to the determination of sulphur in other roasted ores besides those of zinc, for example, pyrites cinders, copper ores, etc., where the sulphides and sulphates are easily decomposed by air and heat.

CONCLUSIONS.

1. The method is very rapid, less than ten minutes being required from taking the sample to completing the titration and calculation.

2. The results are sufficiently accurate for control work in the operation of the plant.

3. The operations are all so simple that they may be entrusted to boys with but little training in chemical manipulation.

DEPUE, ILL.

JAMAICA CAMPHOR.

By H. W. Emerson and E. R. Weidlein

Received November 1, 1911

Up to the time of the Japanese-Russian war, the growth of the *Laurus camphora* outside of the control of the Japanese government for industrial purposes was unknown. On account of the existing high prices of camphor during the war, and the continuation of these high prices, afterwards, a stimulus for the extension of the camphor industry was furnished. It therefore became evident that we must soon depend upon synthetically prepared camphor or look for new fields in which the camphor can be cultivated. The former was naturally the first to supply the needs of the time, but the latter proposition was also taken up and is just beginning to show the great advantage it possesses.

Camphor has been prepared synthetically for a number of years. However, on account of the constantly increasing cost of the raw materials, pinene and crude turpentine, the synthetic preparation of camphor has never proved a paying undertaking.

The objects of this investigation are to determine the quality and amount of camphor and oil that can be obtained from leaves and twigs of camphor trees growing in Jamaica.

The method for determining the yield of camphor was to place weighed camphor leaves in a large galvanized iron can, about two feet high and one and one-half feet in diameter, and containing a false bottom of copper gauze, four inches above the stationary bottom. Steam distillation was carried on for about two hours, at the end of which time the leaves were exhausted. A number of experiments were carried on to determine the time necessary for the complete exhaustion of the leaves, and it was found that the odor of the distillate was an accurate indicator as to whether the leaves were exhausted or not. Long distillations caused a decomposition which gave the distillate a peculiar, unpleasant odor, which was very difficult to remove. The steam, together with the camphor in the vapor form, was led through a large condenser, connected with a two-liter balloon flask, which was surrounded by running water, and this in turn was connected with a second condenser, leading into a large bottle filled with alcohol. Almost all the camphor was condensed in the balloon flask, but a very little passed over and was condensed in the second condenser. The camphor, together with the oil, was collected on the water, as it is soluble in water to the extent of only one part to one thousand, and was separated from the water by filtration. The camphor in this form was a heavy brownish-white substance containing oil and other impurities.

There was sent to us a total of 787.5 pounds of leaves, twigs, trunk and roots and as we received it it weighed 620.25 pounds, making a loss of 21.2 per cent. during transportation.

Sack No. I was labeled "Green Leaves" and was marked "weight 149 pounds." It weighed when we received it 109 pounds, and it had lost 26.8 per cent. of its weight in transportation, due largely to drying.

Table I.—Sack No. I.

Leaves. Grams.	Crude camphor and oil. Grams.	Per cent.
2,000	54.09	2.7
5,000	119.00	2.4
2,000	44 5	2.2
5,000	130.0	2.6
2,000	42.0	2.1
5,000	105 0	2.1
2,000	45.0	2.3
5,000	132.0	2.6
28,000	671 5	2 4

This was the best sack of green leaves and gave a little higher per cent. of camphor.

Sack No. II labeled "Green Leaves" weighed 135 pounds, but when we received it it weighed 99 pounds, a loss of 26.6 per cent.

Table II.—Sack No. II.

Leaves. Grams.	Camphor and oil. Grams.	Per cent.
2,000	23 0	1.2[1]
2,000	30 5	1.52[1]
5,000	93 5	1 87[1]
2,000	38.0	1 90
2,000	38.0	1.90
5,330	137.0	2.57
18,330	360 0	1.82

This was a sack of wettest leaves and the leaves were mildewed considerably, and this seems to decrease the percentage of camphor more than would be accounted for by the increased moisture. The mildew possibly causes the breaking up of the cells which contain the camphor and which seem to hold it quite effectively during ordinary drying.

Sack No. III weighed 82 pounds when shipped and 58 pounds when received, a loss of 29.3 per cent. during transportation.

Sack No. IV weighed 45.5 pounds when shipped and 33.25 pounds when received, a loss of 27 per cent. *Sacks Nos. III and IV were used together.*

Table III

Leaves. Grams.	Camphor and oil. Grams.	Per cent.
1,500	30.0	2.0
2,000	39.5	1.98
2,000	39.0	1.95
2,000	46.5	2.33
2,000	40.0	2.00
2,000	41 8	2 09
2,000	48.0	2 4
140 (500 leaves)	3.0	2.1
2,000	62.0	3.1
2,000	59.5	2.98
2,000	60 0	3.00
19,640	469 3	2.38

The difference in the per cent. yield as noted in the leaves was largely due to the difference in moisture contained by them, which ranged from 25 per cent. in the leaves, on the outside of the sack, to 40 per cent. in the wet leaves in the center of the sack.

The weight expressed as crude camphor in the above three tables is a mixture of gum camphor, oil of camphor and water. The condensed camphor

[1] Omitting because of leaks and using only those in which there was no known loss of camphor gives an average of 2.27 per cent.

and oil of camphor was filtered through a cotton plug and the camphor containing the oil of camphor thus separated from the water. No attempt was made to separate the camphor contained in this saturated water. It was used in refilling the steam chamber and in moistening the leaves in the still.

SUMMARY OF THE CAMPHOR AND OIL IN THE GREEN LEAVES.

TABLE IV

Leaves Grams	Crude camphor and oil Grams.	Per cent.
19,640	469.3	2.38
9,350	213.0	2.27
27,950	671.5	2.40
56,940	1353.8	2.35

ON REMOVING THE OIL FROM THE CAMPHOR.

The mixture of crude camphor and oil of camphor, containing some water, was separated by placing it in cotton sacks in a hand press and subjecting to pressure. The fluid thus forced out consisted of oil of camphor and water. The residue was a white crystalline camphor. The camphor was purified, by mixing with charcoal and slaked lime, and sublimed. The oil was separated from the water by means of separating funnels and Table V gives the result of this purification.

CAMPHOR FROM GREEN LEAVES.

TABLE V.

Per cent	
1.32	pure camphor
0.54	oil of camphor
0.38	water
0.11	loss in manipulation and impurities.
2.35	

CAMPHOR FROM DRIED LEAVES.

Sack V contained when shipped 99 pounds and when we received it 94 pounds, a loss of 5 per cent.

TABLE VI.

Leaves. Grams.	Camphor and oil. Grams.	Per cent.
6,000	160	2.66
6,000	142.0	2.36
2,500	70.0	2.80
6,000	176.0	2.93
20,500	548.0	2.69

Sack VI weighed when shipped 77 pounds and when received 65 pounds, a loss of 15.6 per cent.

TABLE VII.

Leaves Grams	Camphor and oil. Grams.	Per cent.
2,000	38.0	1.90
5,000[1]	70.0	1.40
2,000	48.0	2.40
5,000	100.0	2.00
5,000	133.0	2.66
2,000	54.5	2.73
21,000	443.5	2.08

[1] Omitting because of leak in the still 16,000 grams of leaves, 373.5 grams of camphor and 2.33 per cent. of oil.

Sack VII weighed when shipped 100 pounds and when received 95 pounds, a loss of 5 per cent.

TABLE VIII — SACK NO. VII.

Leaves. Grams	Camphor and oil. Grams	Per cent.
5,000	125.0	2.50
2,000	44.0	2.20
5,000	135.0	2.72
2,000	48.0	2.40
5,000	126.0	2.52
2,000	55.0	2.75
5,000	140.0	2.80
2,000	154.0	2.70
2,500	70.0	2.80
30,500	798.0	2.60

SUMMARY OF RESULTS OF DRIED LEAVES.

Removing the oil and water from the crude camphor the three fractions gave the following results:

TABLE IX.

Leaves. Grams	Camphor and oil. Grams.	Per cent.
20,500	548.0	2.69
16,000	373.5	2.33
30,500	798.0	2.60
67,000	1719.5	2.54

TABLE X.

Grams.		Per cent.
600 grams gave	365 camphor	60.83
	110 oil	18.33
	120 water	20.00
	5 loss	0.84

TABLE XI.

Grams.		Per cent.
500 grams gave	305 camphor	61.00
	90 oil	18.00
	95 water	19.00
	10 loss	2.00

TABLE XII.

Grams.		Per cent.
600 grams gave	380 camphor	63.33
	105 oil	17.5
	105 water	17.5
	10 loss	1.67

The 2.54 per cent. of crude camphor is made up as follows:

TABLE XIII.

Per cent.	
1.569	pure camphor
0.457	oil
0.482	water
0.031	loss in manipulation and impurities.
2.54	

A comparison of the results between the camphor yield in the wet and dried leaves is unfortunately only of comparative value because, as noted before, the green leaves had dried more or less in shipment and the dried leaves were not thoroughly dried, but were assayed as sent to determine the best time to harvest the leaves. The results indicate that there is very little or no loss of camphor during ordinary weather drying, but that the cells of the leaves hold quite securely the gum camphor. This is important as it makes possible an economical harvesting of

the leaves. The leaves may be left to fall and can be gathered at convenient intervals.

The dried leaves contain proportionately less oil of camphor and more camphor than the green leaves. This is probably due to an accelerated oxidation of oil of camphor during the last stages of life in the leaves.[1] This also shows that the camphor is so well enclosed in the vegetable cells that it is not easily dispensed. This is further substantiated by the fact that the dead leaves still contain a considerable quantity of camphor.

The dead leaves weighed 12 pounds when shipped and 7.5 pounds when received, making a loss during transportation of 37.5 per cent. This marked loss in weight of the dead leaves is entirely unexpected.

2730 grams of dead leaves (leaves from a dead tree) yielded 38 grams of camphor or 1.39 per cent. This is less than the yield from green or dried leaves and this camphor contained very little oil of camphor.

CAMPHOR IN THE TWIGS FROM GREEN LEAVES.

TABLE XIV.

Twigs. Grams.	Camphor and oil. Grams.	Per cent.
2.275	24.15	1.06
2.800	22.00	0.81
2.800	38.00	1.36
4.000	51.00	1.27
10.550	138.00	1.30
22.425	273.15	1.16

TABLE XV.

Grams.		Per cent.	
136.609	camphor	50	camphor
60.28	oil	22	oil
61.24	water	22.4	water
15.03	loss	5.0	loss

The green twigs then yielded:

TABLE XVI.

Per cent.	
0.580	camphor
0.255	oil of camphor
0.260	water
0.065	loss

TWIGS FROM DRIED LEAVES.

8770 grams of twigs yielded 0.84 gram of crude camphor and 46.2 grams of pure camphor = 0.5445 per cent. camphor.

CAMPHOR FROM WOOD.

1800 grams of wood yields 11 grams of camphor; 0.61 per cent of camphor.

The camphor thus obtained is a white crystalline substance. When first taken from the press it has a melting point of 175.5° C. and upon resubliming and crystallizing from petroleum ether it melts at 177° C. and boils at 204.5°. It is dextrorotatory 42.82°. Specific gravity 0.980.

The properties of camphor required by the U. S. P. are as follows:

Melting point	174° C.
Boiling point	204° C.
Specific gravity	0.990
Dextrorotatory	41°

[1] *J. Soc. Chem. Ind.*, **21**, 1036

The above analyses indicate this to be a good, pure gum camphor possessing all the properties required by U. S. P.[1]

The oil obtained from the green leaves was fractionated as follows:

TABLE XVII.

	Degree	Per cent
Boiling point...	158–165	11.2
	165–173	14.5
	173–178	9.285
	178–190	10.20
	190–195	5.45

TABLE XVIII.

	Degrees.	Per cent.	
Boiling point...	195–205	12.9	15.2 per cent. camphor obtained from these fractions.
	205–228	21.1	
	228–240	5.45	
	240–255	3.63	
	Residue.	1.82	

The oil from the dried leaves gave the following results:

TABLE XIX.

	Degrees.	Per cent.
Boiling point...	158–175	7
	175–185	19
	185–195	20
	195–205	20
	205–220	10
	220–240	10
	240–252	5
	Residue.	9

After several fractionations the following fractions were obtained:

TABLE XX.

Boiling point...	158–170	9.3	
	170–175	10.3	
	175–185	21.7	
	185–195	7.0	
	195–205	24.4	camphor
	205–215	6.3	separated
	215–230	7.7	
	230–235	2.7	
	235–240	1.3	
	240–260	2.3	
	260–280	2.3	
	Residue.	6.4	

TABLE XXI.

	Degrees.	Per cent.
Boiling point...	150–195	41.5
	195–220	41.5
	220–245	8.5
	Residue red oil,	8.5

The oil has a specific gravity of 0.915.

400 cc. of the oil obtained by combining fractions which distilled at the same temperature were redistilled with the following results:

TABLE XXII.

	Degrees.	Cc.	Per cent.	Specific gravity.
I.	158–165	20	5	0.844
II.	165–173	76	19	0.860
III.	173–178	43	10	0.870
IV.	178–192	56	14	0.899
V.	192–202	8	2	0.915
(V_a)	Camphor 101 grams		25	
VI.	202–215	26	6.5	0.924
VII.	215–228	20	5.0	0.928
VIII.	228–236	18	4.5	0.931
IX.	236–252	16	4.0	0.933
X.	Residue	20	5.0	
			100.0	

[1] Pharmacopoeia of the United States, Eighth Decennial Revision, p. 88.

V and VI are the results of six fractionations distilling between 192° 215° and freezing out successively.

88 grams of camphor
26 grams of camphor
14 grams of camphor
6 grams of camphor

101 (Va)

Thus from 400 cc. of oil of camphor from the Jamaica leaves we obtained 101 grams of camphor or 25.25 per cent. of camphor.

Comparing the analysis of the oil obtained from Jamaica camphor with that as published in Schimmel[1] we have the following:

TABLE XXIII

	Degrees.	Jamaica. Per cent.	Schimmel. Per cent.
Boiling point..	175–180	34	26–38
	180–185	14	30–44
	185–190	7	11–19
	190–215	31	10 camphor
	215	18.5	4 safrol and eugenol.

The last three constituents are valuable.

The oil as first obtained in pressing the camphor is a colorless liquid, which soon turns yellow on exposure to the air. The first fractions are colorless and transparent and have a specific gravity of 870–910. These distil between 150–195°. The chief constituents are pinene, phellandrene, cineol, dipentene and some camphor. On further fractionating, a yellow and a red oil are obtained. The camphor is separated out from the yellow oil and safrol from the red oil.

From this report, it is evident that the determinations are almost all made from the leaves which in all cases were richer in camphor than the wood. However, the percentage of camphor contained in the leaves, with the cheap labor and the good methods for obtaining the camphor and oil, which has been found to possess equal properties with the best camphor placed on the market, renders possible the industry of camphor in Jamaica. This can be accomplished by harvesting the leaves only, thus allowing the trees to grow and become larger, more vigorous, and consequently more valuable each year.

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THE INDEX OF REFRACTION OF THE MIXED ACIDS OF FATTY OILS.

By W. B. SMITH.

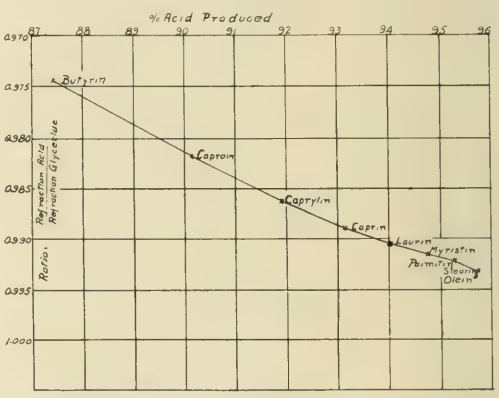
Received November 1, 1911.

This study was begun because of the anomalous figures given by Lewkowitsch,[2] Allen[3] and Van Nostrand,[4] for the index of refraction of the mixed acids of rape oil and cocoa butter. Without doubt these are typographical errors, 1.4991 instead of 1.4491[1] for rape oil at 60°, and 1.422 instead of 1.442[1] for cocoa butter. It seemed worth while, however, to find, if possible, a general formula for this constant and the following is offered as the solution:

TABLE I.—RATIO OF ACIDS TO GLYCERIDES

Tri-glyceride.	Refractive Index. Glyceride.	Acid.	Temp. °C.	"Refraction ratio." acid/ glyceride.	Produced from glyceride. Acid. Per cent.	Glycerol. Per cent.
Butyrin.....	1.43587	1.39906	20	0.9744	87.44	30.46
Caproin.....	1.44265	1.41635	20	0.9817	90.16	23.96
Caprylin.....	1.44817	1.42825	20	0.9862	91.91	19.58
Caprin.....	1.44461	1.42855	40	0.9889	93.14	16.67
Laurin.....	1.44039	1.42665	60	0.9905	94.04	14.42
Myristin.....	1.44285	1.43075	60	0.9916	94.75	12.74
Palmitin.....	1.43807	1.42693	80	0.9922	95.29	11.42
Stearin.....	1.43987	1.43003	80	0.9932	95.73	10.34
Olein	1.4636	1.4546	40	0.9938	95.70	10.41
Linolin.....	...	...	..	(0.9935) ?	95.67	10.48
Linolenin.....	...	...	..	(0.9935) ?	95.63	10.55

There have been collated in Table I the refractive indices of triglycerides and their corresponding acids, as given by Lewkowitsch, as well as the amounts of fatty acid and of glycerol produced on hydrolysis, and from these data has been calculated the ratio of the refractive index of the acid to that of the glyceride. By comparing these figures and from the curve



shown it is seen that this ratio depends upon the percentage of acid in the glyceride. The irregularities in the curve may be due to the differences of the temperatures of reading.

It is seen that the "refraction ratios" of stearin and olein are practically the same. As linolin and linolenin have nearly the same percentage composition as stearin and olein, there is no reason to doubt that their "refraction ratio" is not much different. Hence, it is reasonable to suppose that the refractive index of the mixed insoluble acids of the fatty oils may be closely calculated by multiplying the refractive index

[1] Schimmel & Co., Allen's "Organic Analysis," Vol. II, Part III, p. 804.

[2] "Oils, Fats and Waxes," **1904**, 563, 728, 196; **1909**, II, 202, 481; I, 411.

[3] "Organic Analysis," 3rd Ed., **2**, 137, 166; 4th Ed., **2**, 124, 178.

[4] *Chemical Annual*, **1909**, 60, 63.

[1] Thoerner, *J. Soc. Chem. Ind.*, **1895**, 43.

Other errors noted: Index of refraction of black mustard oil, 1.4672 at 15.5°, *Lewk.*, **1904**, 572; **1909**, II, 214: Van Nostrand, p. 58: given by Tolman, *Bull.* **77**, Bureau Chemistry, p. 45, as 1.4762.

Allen, 3rd Ed., p. 72, 4th Ed., p. 43, gives 0.000176 instead of 0.000365 as the factor for correction for temperature.

Lewkowitsch, **1904**, 196; **1909**, I, 411, should read for the refraction of the oils themselves: cocoanut oil, 1.441; lard, 1.4539; beef tallow, 1.4510; mutton tallow, 1.4501.

of the oil by 0.9938, the ratio of oleic acid to olein. A preponderance of laurin, myristin, or palmitin should lower this factor.

To test this hypothesis the published data was examined, and the best of it is given in Table II.

The greater number of these figures give "refraction ratios" not greatly different from 0.9938. Some, however, vary considerably from this, and consequently experimental data appeared desirable. A number of oils were procured from as reliable sources as was convenient. Rapeseed oil was extracted from the seed by ether and corn oil from yellow maize in the same way. The linseed, cod liver, peanut and olive oils and cocoa butter were purchased from trustworthy dealers, hence, although showing no evidences of adulteration are not guaranteed to be absolutely pure. The other oils were obtained from known sources.

Separation of the acids was performed by saponifying with alcoholic soda, boiling off the alcohol, dissolving in water, treating with dilute H_2SO_4, separating the oily layer and drying and filtering if necessary. Drying was curtailed as much as possible to avoid oxidation. The refractive index was determined on an Abbe-Zeiss refractometer with heatable prisms, a temperature of 40° being used except where the fats were solid at this temperature. The oil and acids in each case were read at the same temperature, and when necessary corrected to 40° by the use of the factor 0.000365, the error being negligible within short ranges of temperature. The results are shown in Table III.

Owing to the danger of oxidizing the acids if dried too long, the refractive indices of the acids are probably accurate to only about three units in the fourth decimal place. The oils themselves are more nearly correct.

The ratio for peanut oil is no doubt high because of the depression of the refraction of the oil due to the large amount (11 per cent.) of free acid present. Excluding this, the nine liquid oils range from 0.9933 to 0.9942, the average being 0.99376. Although only a few samples were examined, the closeness of the result to the factor derived from Table I indicates that it is correct, while the variety of oils tested would show that it is of general application. The nine samples of solid fats range from 0.9941 to 0.9923, averaging 0.9932. The lower acids were evidently washed out of the butter. The other fats show a lower factor in proportion as they contain much palmitin, myristin or laurin.

The last column in Table III shows refractive indices of other observers calculated to 40°, excluding the incorrect figures on rape oil and cocoa butter. The

TABLE II.—PUBLISHED DATA.

Oil.	Index of refraction. Oil.	Acids.	Temp.	"Refraction ratio."	Authority.
Linseed	1.4660	1.4546	60	0.9922	Thoerner
Linseed	1.480	1.472	20	0.9946	Jensen
Cod liver	1.4621	1.4521	60	0.9932	Thoerner
Soy bean	1.4718	1.4650	27.5	0.9954	Oettinger and Buchte
	1.4728	1.4655	27.5	0.9950	Oettinger and Buchte
Rapeseed	1.4667	1.4491	60	0.9880	Thoerner
	1.4667	1.4991 (?)	60	1.0221	Allen
Castor	1.4636	1.4546	60	0.9939	Thoerner
Sunflower	1.4611	1.4531	60	0.9945	Thoerner
Poppyseed	1.4586	1.4506	60	0.9945	Thoerner
Cottonseed	1.4570	1.4460	60	0.9902	Thoerner
11 samples Max.	1.4654	1.4567	40	0.9941	Wagner and Clement
11 samples Min.	1.4647	1.4552	40	0.9934	Wagner and Clement
11 samples Av.	1.4649	1.4557	40	0.9937	Wagner and Clement
Sesame	1.4561	1.4461	60	0.9931	Thoerner
	1.4651	1.4559	40	0.9937	Utz
Almond	1.4555	1.4461	60	0.9935	Thoerner
	1.4674	1.4589	40	0.9942	Ross and Race
Apricot kernel	1.4674	1.4590	40	0.9943	Ross and Race
Peach kernel	1.4630	1.4558	40	0.9950	Ross and Race
Almond, Java	1.4602	1.4512	40	0.9938	Pactrovitch
Peanut	1.4545	1.4461	40	0.9942	Thoerner
Olive	1.4548	1.4410	60	0.9905	Thoerner
Cashew nut fat	1.4545	1.4459	60	0.9941	Smith and Clark
Lard (fat)	1.4539	1.4395	60	0.9901	Thoerner
Lard, very oily	1.4541	1.4450	60	0.9931	Richardson
Lard, American	1.4594	1.4500	40	0.9936	Arnold
Lard, German	1.4578	1.4484	40	0.9936	Arnold
Lard, German	1.4582	1.4481	40	0.9931	Arnold
Chicken	1.4576	1.4499	50	0.9947	Ross and Race
Turkey	1.4565	1.4470	50	0.9935	Ross and Race
Rabbit	1.4587	1.4495	40	0.9937	Lewkowitsch
Palm	1.4510	1.4441	60	0.9952	Thoerner
Tallow, beef	1.4510	1.4375	60	0.9907	Thoerner
Tallow, mutton	1.4501	1.4374	60	0.9912	Thoerner
Butter	1.445–1.448	1.437–1.439	60	0.9945–0.9938	Thoerner
Butter	1.4550	1.4470	40	0.9945	Arnold
Margarin	1.453	1.444	60	0.9938	Thoerner
Cacao butter	1.4496	1.442	60	0.9948	Thoerner
	1.4496	1.422 (?)	60	0.9810	Allen
Palmnut	1.4431	1.4310	60	0.9916	Thoerner
Cocoanut oil	1.4410	1.4295	60	0.9920	Thoerner

result obtained by Thoener on olive oil does not seem admissible, as the refractive index of oleic acid, which forms 75 to 90 per cent. of the fatty acids, is 1.4471 at 60°, or 1,4546 at 40°. If we take as a basis for calculation the index of refraction of linolic acid as approximately 1.4643 at 40° and the composition of the fatty acids of an olive oil as 10 per cent. palmitic acid, 84 per cent. oleic and 6 per cent. linolic, the refractive index of the mixture is about 1.4539 at 40°, while Thoerner's figure of 1.441 at 60° is about 1.4483, against the value on Table III of 1.4528.

TABLE III.—EXPERIMENTAL RESULTS.

	Index of refraction.		"Refraction ratio."	Refractive index mixed acids, other observers, calc. to 40°.
Oil.	Oil.	Acids.		
Linseed oil	1.4734	1.4635	0.9933	1.4619–1.4647
Cod liver oil	1.4711	1.4625	0.9942	1.4594
Soy bean oil	1.4682	1.4586	0.9935	1.4610
Corn oil[1]	1.4677	1.4583	0.9936	1.4585
Corn oil[2]	1.4675	1.4585	0.9939	1.4585
Rapeseed oil	1.4658	1.4572	0.9941	1.4564
Cottonseed oil	1.4637	1.4545	0.9937	1.4533–1.4567
Peanut oil	1.4633[3]	1.4552	0.9947	1.4534
Olive oil	1.4619	1.4528	0.9938	1.4483
Lard	1.4590	1.4491	0.9932	1.4468–1.4500
Lard stearin (very soft)	1.4585	1.4487	0.9933	....
Oleo oil	1.4578	1.4479	0.9932	(tallow 1.4447–1.4448)
Cocoa butter	1.4563	1.4475	0.9939	1.449
Butter (renovated)	1.4544	1.4458	0.9941	1.444–1.447
Oleostearin	1.4549	1.4437	0.9923	(tallow 1.4447–1.4448)
Palmnut oil	1.4496	1.4392	0.9928	1.4383
Cocoanut oil	1.4494	1.4386	0.9925	1.4368
(80% cottonseed) (20% oleostearin)	1.4624	1.4527	0.9934	....

Effect of Unsaturated Acids.—The data given in this paper show that the iodin value and the higher refraction of unsaturated acids, due to double and triple linkages, do not effect this factor materially. As the iodin value and the refraction of the acids increase, those of the glycerides increase also. The difference between the refraction of the glycerides and of the acids, averaging 0.0092 for fatty oils, is so small in comparison with the total refraction that the absolute refraction has little effect on the factor. The extremes of 1.5 and 1.4 would give $\frac{1.4908}{1.5000}$ = 0.9939 and $\frac{1.3908}{1.4000}$ = 0.9934. This is, of course, true only of these oils. The relation between iodin value and this factor is shown in Table IV.

TABLE IV.—EFFECT OF UNSATURATION.

	Index of refraction.		Temp.		Iodin no. (Estimated.)	Per cent. unsaturated acids.
	Glyceride.	Acid.	Degrees.	Factor.		
Olein	1.4563	1.4471	60	0.9937	86.2	100
Stearin	1.4472	1.4373	60	0.9932	0.0	0
Linseed oil	1.4734	1.4635	40	0.9933	185	90
Corn oil	1.4677	1.4583	40	0.9936	120	92
Olive oil	1.4619	1.4528	40	0.9938	85	90
Lard	1.4590	1.4491	40	0.9932	62	70
Oleo oil	1.4578	1.4479	40	0.9932	50	55
Cocoa butter	1.4563	1.4475	40	0 9939	35	40

[1] Extracted in laboratory.
[2] Outside source.
[3] Eleven per cent free acid

Here there is, with olein and stearin, a difference in refraction of 0.0091, of iodin value of 86.2, and in saturation of 100 per cent., yet the factor is about the same. With the oils given, which consist very largely of glycerides of acids of eighteen carbon atoms, but which differ widely in refraction, iodin value, and saturation, the variation in the factor is within the limits of error.

CONCLUSIONS.

1. The values 1.4991, 1.422 and 1.441 for the refractive indices at 60° of the insoluble acids of rape oil, cocoa butter and olive oil, respectively, are not correct.

2. The relation between the refraction of the oil and the refraction of the acids depends upon the percentage of acid in the glycerides, being nearly independent of the total refraction and of the iodin value.

3. The refractive index of the insoluble acids of fatty oils should be close to the refractive index of the oil multiplied by 0.9938.

4. For solid fats this factor should lie between 0.992 and 0.994, according to the composition of the fat.

LABORATORIES U. S. BUREAU OF ANIMAL INDUSTRY.

THE CHLORINE CONTENT OF MILK.[1]

By PAUL POETSCHKE.

Received October 29, 1911.

In a previous publication[2] concerning the determination of sodium chloride in milk, the author gave preliminary consideration to the ratio existing between ash and sodium chloride as a means of detecting added salt. The present paper is the result of an extended study of this ratio.

All of the chlorine determinations recorded in this paper were made by the author's method. Briefly, this consists in removal of the fat and proteids with copper sulphate and sodium hydroxide. The filtrate is acidified with nitric acid and titrated by Volhard's method.

Total solids were determined with the aid of a special pipette[3] devised to deliver five grams of milk. The lactometer readings recorded in all of the present work were taken with the instrument described in the same paper on total solids. Fat was determined by the Babcock method. Incinerations for ash were made in a muffle, care being taken to prevent the platinum dishes from being heated to visible redness.

Richmond[4] states that the chlorides in milk can be titrated with silver nitrate, using potassium chromate as indicator, and that 10 cc. of milk took on an average 3.45 cc. $N/10$ silver nitrate with extremes of 3.35 and 3.6 cc. in nine samples.

It is well known that phosphates interfere with the determination of chlorine by this method. In the case of milk, a proper end point can not be obtained.

[1] Read before N. Y. Section, October, 1911.
[2] THIS JOURNAL, **2**, No. 5.
[3] *Ibid.*, **3**, No. 6.
[4] *Analyst*, **34**, 208.

Instead of changing to a reddish color when all of the chlorine is converted to silver chloride, a yellow color, gradually becoming deeper and developing into orange, is noted. A reddish color is observed only after a considerable excess of silver nitrate is present.

In Table I is given the results obtained by direct titration with silver nitrate using potassium chromate as indicator. The results obtained with the author's method are given for comparison.

The direct titrations with chromate indicator were made on 10 cc. of milk, with and without dilution. In each case the same amount of indicator was used and the titration continued until the first change to a deeper yellow was noted. The milk, containing the same amount of indicator, was used as a control to note the first change in color.

TABLE I.—SODIUM CHLORIDE IN GRAMS PER 100 CC.

Direct titration with chromate indicator.

Number	10 cc. undiluted.	10 cc. diluted with 90 cc. of water.	Author's method.
71,884	0.246	0.324	0.180
71,885	0.238	0.276	0.167
71,888	0.248	0.315	0.183
71,900	0.167	0.334	0.194

These results show that direct titration of milk with silver nitrate, using potassium chromate as indicator, is impossible. Richmond fails to give any data concerning the accuracy of the direct titration. The five experiments which he records, showing "salt added" and "salt found," may be correct in so far as the added salt is concerned, provided the titration is carried to the same end point as the original milk. This is no proof whatever that the chlorine in milk can be determined by direct titration.

Milk from individual cows may vary greatly from the normal. Certified milk offers an opportunity to study the mixed milk of healthy cows. Such milk is produced under the regulations of a medical or scientific milk commission or else inspected by law.

Table II gives the results obtained on ten samples of certified milk.

TABLE II.

Number.	Total solids.	Fat.	Proteids.	Lactometer at 60° F.	Ash	Sodium chloride.	Ratio ash/sodium chloride.
57,025	12.50	3.60	3.28	115	0.781	0.181	4.31
53,989	12.18	3.60	..	111	0.730	0.158	4.62
53,990	12.24	4.10	.	105	0.725	0.205	3.54
58,037	14.40	4.90	..	121	0.739	0.111	6.66
67,526	13.05	4.60	2.66	105	0.693	0.154	4.50
64,304	14.01	5.50	3.25	104	0.740	0.200	3.70
68,808	12.74	4.00	..	112	0.745	0.143	5.21
71,617	12.54	3.90	3.22	110	0.790	0.195	4.05
a.	...	..	..	...	0.729	0.163	4.47
b.	...	..	.		0.759	0.186	4.08
Maximum	...	..	..	..	0.790	0.205	6.66
Minimum	...	..	..	..	0.693	0.111	3.54
Average					0.743	0.170	4.51

Table III gives the results obtained on twenty-two samples of market milk.

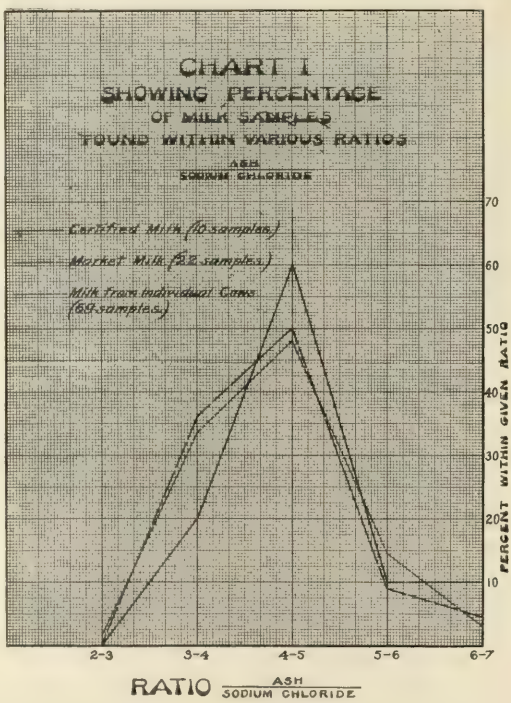
The sixty-nine samples of milk, recorded in Table V, are from individual cows. As far as it was possible to ascertain, these samples were taken under conditions which prevented their being watered or otherwise tampered with. It was necessary to preserve

TABLE III.

Number.	Total solids.	Fat.	Lactometer at 60° F.	Ash.	Sodium chloride.	Ratio ash/sodium chloride.
59,604	16.12	6.50	118	0.816	0.180	4.53
65,055	11.81	3.40	110	0.760	0.149	5.10
65,056	11.81	3.40	110	0.760	0.113	6.73
65,057	11.34	3.30	104	0.680	0.158	4.30
65,058	10.77	2.80	104	0.690	0.149	4.63
65,059	11.72	3.40	109	0.720	0.149	4.83
65,060	11.80	3.45	108	0.610	0.153	3.99
64,907	12.17	3.60	112	0.666	0.167	3.97
64,909	12.04	3.60	111	0.716	0.193	3.70
64,910	12.47	3.60	114	0.698	0.180	3.87
64,933	12.78	4.10	112	0.696	0.169	4.12
64,934	12.49	3.80	112	0.720	0.176	4.09
64,935	12.04	3.60	109	0.730	0.159	4.50
64,936	11.63	3.20	110	0.700	0.154	4.54
64,937	12.01	3.40	112	0.726	0.169	4.29
64,938	12.04	3.50	111	0.734	0.154	4.75
64,256	12.46	3.70	.	0.710	0.143	4.96
64,257	12.37	3.60	...	0.710	0.130	5.46
69,190	11.57	3.90	97	0.684	0.220	3.11
69,191	11.38	3.80	96	0.696	0.193	3.62
69,192	10.92	3.65	92	0.705	0.228	3.09
69,193	11.17	3.80	93	0.677	0.206	3.28
Maximum	...	.	...	0.816	0.228	6.73
Minimum	..	..	...	0.610	0.113	3.09
Average				0.709	0.168	4.34

these samples. Formaldehyde was added in the proportion of about 1 to 2000.

An experiment was made to determine whether formaldehyde in any way interfered with the determination of chlorine. A sample of milk was treated with formaldehyde (approximately 40 per cent.)



in the proportion of 1 to 1000 and 1 to 500. Chlorine was determined in the original and treated samples.

The results given in Table IV show that, even in this unusually large proportion of formaldehyde, no error is introduced.

TABLE IV.

		Sodium chloride. Per cent.
Original sample	*a.*	0.144
	b.	0.143
Treated with 1 1000 formaldehyde	*a.*	0.147
	b.	0.142
Treated with 1 500 formaldehyde	*a.*	0.144
	b.	0.144

TABLE V.

Number.	Total solids	Fat	Lactometer at 60° F.	Ash.	Sodium chloride.	Ratio ash/ sodium chloride.
68,344	13.01	4 60	105	0.756	0.184	4.11
68,345	12.66	4 20	109	0 740	0.170	4 35
68,346	12.79	4 00	111	0 750	0.197	3 81
68,347	11 89	3 60	107	0.686	0.177	3.87
68,348	12.62	3.75	115	0.840	0.190	4 42
68,349	11.68	3.70	101	0 658	0.204	3.23
68,350	12.18	3 40	113	0.730	0.181	4.03
68,351	14.73	5 50	114	0.736	0.143	5.15
68,352	11.41	3.20	106	0 800	0.232	3.45
68,353	13.33	4.85	107	0.750	0.170	4.41
68,354	11.67	3.45	106	0 700	0.175	4 00
68,355	14.18	4.90	...	0.720	0.196	3.67
68,356	11.37	3.30	104	0 736	0.198	3 72
68,357	11.63	3.20	109	0.762	0.166	4 59
68,358	13.05	4.20	113	0.732	0.132	5.55
68,359	12.30	3 80	108	0 786	0.186	4 22
68,360	12.57	4 40	102	0.670	0.180	3 72
68,361	13.64	4 40	...	0 730	0.134	5.45
68,362	12.55	3.80	...	0 800	0.203	3.94
68,363	11.17	3 20	104	0.750	0.216	3.47
68,364	12.72	3 60	. .	0.720	0.171	4.21
68,365	12.81	4.00	...	0 694	0.178	3 90
68,366	12.99	4 65	104	0 750	0.185	4 05
68,367	12.21	3 60	111	0.748	0.150	4.99
68,368	12.17	3 60	111	0.734	0.164	4.48
68,369	14.75	6.10	107	0 730	0.186	3 93
68,370	10.87	3.20	100	0 704	0.222	3.17
68,371	11.47	3.40	104	0.796	0.209	3.81
68,372	12.19	4.00	104	0.700	0.181	4.09
68,373	12.66	4.20	106	0.778	0.174	4.47
68,374	13.26	4 30	114	0 740	0 146	5.07
68,375	12.21	3.80	108	0 666	0.164	4.06
68,376	14.43	4.60	125	0.928	0.212	4 38
68,377	13.73	4.80	111	0.736	0.157	4 69
68,378	14.49	5.60	109	0.740	0.173	4.28
68,379	11.29	3.40	102	0.726	0.216	3.36
68,380	12.19	3.40	113	0.730	0.140	5.21
68,381	11.09	3.00	105	0.724	0.185	3.91
68,382	11.57	2.80	114	0.710	0.155	4.58
68,383	11.10	2.70	111	0.780	0.131	5.95
68,384	12.52	3.60	115	0.632	0.147	4.30
68,385	12 63	4.00	112	0 634	0.157	4.04
68,386	12.93	4.30	109	0.670	0.152	4.41
68,387	11.73	3.60	103	0.616	0.174	3.54
68,388	11.22	2.50	117	0.662	0.138	4.80
68,389	12.50	3.80	111	0.710	0.141	5.03
68,390	11.02	2.95	105	0.706	0.197	3 58
68,391	12.39	3.70	111	0.720	0.128	5.62
68,392	12.03	3.40	111	0.710	0.154	4.61
68,393	10.92	2.50	111	0 774	0.161	4.80
68,394	12.03	3.70	106	0.720	0.157	4.59
68,395	13.08	4.10	114	0.730	0.148	4.93
68,396	11.49	3.60	102	0.790	0.241	3.28
68,397	11.41	2.90	112	0 690	0.165	4.18
68,398	12.56	3.40	...	0 690	0.127	5.43
68,399	9.75	2.60	...	0.820	0.335	2.45
68,400	11 64	3.50	104	0.700	0.184	3.80
68,401	12.30	3.90	106	0 704	0 196	3 59
68,402	11.74	3 60	106	0.710	0.174	4.08
68,403	9.78	2.40	97	0.730	0.228	3 20
68,404	11.46	2 80	116	0.720	0.176	4.09
68,405	10.88	2.60	111	0.772	0.203	3.80
68,406	11.73	3.40	107	0 758	0.162	4.68
68,407	11.15	2.30	118	0.710	0.143	4.97
68,408	11.82	3.00	118	0.720	0.116	6 20
68,409	12.18	3 60	112	0.726	0.126	5.76
68,410	9.70	3 40	80	0 532	0.145	3 67
68,411	11.77	3 50	108	0 720	0 152	4 74
68,412	13 93	4 90	114	0.742	0 112	6.63
Maximum	...	..	...	0 928	0 335	6.63
Minimum	. .			0 532	0 112	2.45
Average				0.728	0.173	4.33

Several samples of milk, found to contain large amounts of added salt, are given in Table VI. These samples were all very salty to the taste. Evidently the salt was added in these cases by persons who sought to satisfy a personal grudge against the dealer or consumer. The samples were received for examination for foreign substances.

TABLE VI.

Number.	Total solids.	Fat.	Lactometer at 60° F.	Ash.	Sodium chloride.	Ratio ash/ sodium chloride.
64,908	12.23	3.40	118	0.780	0.415	1.88
49,383	12.10	3.50	117	1.140	0.615	1.85
67,819	14.84	5.80	...	3.160	2.610	1.21

One sample of milk containing both added water and salt is given below. The taste of this sample was not distinctly salty.

SAMPLE NO. 54,284.

	Per cent.
Lactometer at 60° F	81
Total solids	8.00
Fat	2.00
Ash	0.65
Sodium chloride	0.239
Ratio ash/sodium chloride	2.71

Table VII gives the maximum, minimum and average results obtained on certified milk, market milk and milk from individual cows.

TABLE VII.

		Ash.	Sodium chloride.	Ratio ash/ sodium chloride.
Certified milk, 10 samples	Maximum	0.790	0.205	6.66
	Minimum	0.693	0.111	3.54
	Average	0.743	0.170	4 51
Market milk, 22 samples	Maximum	0 816	0.228	6.73
	Minimum	0.610	0.113	3.09
	Average	0.709	0.168	4.34
Milk from individual cows, 69 samples	Maximum	0.928	0.335	6.63
	Minimum	0.532	0.112	2.45
	Average	0.728	0.173	4.33

Table VIII shows the percentage of milk samples found within various ratios of $\frac{\text{Ash}}{\text{sodium chloride}}$.

TABLE VIII.

Ratio ash/sodium chloride	2 to 3	3 to 4	4 to 5	5 to 6	6 to 7
Certified milk, 10 samples	0	20.0%	60.0%	10.0%	10.0%
Market milk, 22 samples	0	36.4%	50.0%	9.1%	4.5%
Milk from individual cows, 69 samples	1.5%	33.3%	47.8%	14.5%	2.9%

The results given in Table VIII, represented graphically in Chart I, show that 90 per cent. of the certified milk samples, 95.5 per cent. of the market milk samples and 95.6 per cent. of the samples of milk from individual cows be within the ratio of 3 to 6. Comparatively few samples fail to come within this range.

It is apparent that the chlorine content of milk is subject to wide variation and that the average chlorine content, expressed in terms of sodium chloride, is 0.17 per cent. The average ratio of $\frac{\text{Ash}}{\text{sodium chloride}}$ is 4.5.

In conclusion I wish to acknowledge my indebtedness to my assistants, Messrs. Carl Marx and J. Schroff, for their assistance in the analytical work.

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NEW YORK CITY.

TEMPERATURE CORRECTIONS IN RAW SUGAR POLARIZATIONS.[1]

By W. D. Horne.

Received November 23, 1911.

In polarizing raw sugars at temperatures other than the standard 20° C., errors are introduced that are of serious moment. Much has been written on the subject and temperature corrections have been worked out, but unfortunately they have not been generally adopted.

One of the best methods of effecting the necessary corrections is that described by Dr. C. A. Browne at the 7th International Congress of Applied Chemistry, to be described later; and the present paper is to present results on many hundreds of analyses, which entirely corroborate the reliability of this method of correction.

In the spring of 1909, when the New York Sugar Trade Laboratory was planned, I made some preliminary experiments on temperature corrections in my own laboratory to ascertain the relative results of polarizing at 20° and at higher temperatures, and later I have made continued close comparisons between the polarizations of the Sugar Trade Laboratory at 20° and polarization of the same sugars in other laboratories at ordinary room temperatures.

In the early experiments it was necessary, for polarizing at 20°: 1, that the solution of the normal weight of sugar should be made up to 100 cc. at 20° C.; 2, that it should be polarized at 20° C.; 3, that the polariscope should be at 20° C.

In order to accomplish these ends I cooled the solution of sugar in a flask with a thermometer in ice-water to 20° C., filling to the mark with a few drops of water at about this same temperature. The solution was then shaken and filtered at room temperature, which necessarily warmed it up a little, as the laboratory was usually above 20° C. This filtrate was put into a tubulated 200 mm. observation tube, containing a centrally located thermometer, and immersed in ice-water until the temperature fell a little below 20° C. (about 18° C.), the tube dried with a towel, two protecting caps containing granular soda lime to prevent condensation of atmospheric moisture on the cold end glasses slipped on, and the whole put into the polariscope. These caps fit tightly over the ends of the observation tube and each has a glass windowed end and an annular space inside filled with soda lime, which was found to be much better for this purpose than calcium chloride or caustic alkali.

The polariscope was kept at 20° C. by enclosing the working parts, including both polarizing and analyzing nichols, in a galvanized iron box covered with a $^5/_8$-inch layer of cork board made by the Armstrong Cork Company, of Pittsburgh, and containing two $^1/_4$-inch copper tubes, running along each side of the inside of the box, through which ice-cold water was circulated.

It was found advisable to pass water at 1° C. through this tube at the rate of 100 cc. per minute, which cooled the polariscope to 20° C. as shown by a thermometer passing through the box and covering, near the analyzer and compensating quartz wedges. The water issued at about 13° C. when the temperature of the room was between 23° and 31° C. The polariscope was maintained at 20° C. about an hour before polarizations were made and the observation tube when inserted at other than 20° quickly came to this standard, a change of as much as two degrees taking place in four minutes.

Cane sugars polarized at temperatures higher than 20° C. are subject to a temperature correction, which may be divided into two parts: 1, the temperature correction for pure sucrose, given by the formula $P.\ 20 = P.^t[1.0 + 0.0003(t - 20)]$ and 2, the temperature correction as applied to pure levulose, the formula being $P.\ 20 = P^t - 0.00812L(t - 20)$. By properly applying the combination of these formulas to a raw cane sugar polarized at temperatures other than 20°, it is possible to arrive at a result very close indeed to that which would be obtained when polarizing the sugars at 20°, as may be seen by the following set of observations, on eight raw sugars, giving the polarizations actually obtained at 20° C. (the polariscope, the solution and containers all being at this same degree), as compared with polarizations of the same sugars at higher degrees, as indicated in Table I. These 95° sugars were assumed to contain 1.25 per cent. invert sugar on the average, and having calculated the corrections for the sucrose and levulose separately and having united all these results, it was found that these corrected polarizations were only 0.0247

Table I.

At 20°	At 26.5.	Diff.	Calculated correction for sucrose alone.	Calculated correction for levulose.	Calculated correction for both levulose and sucrose.	Difference of calculated polarization from actual polarization at 20° C.
95.4	95.3	—0.10	+0.1868	—0.0330	+0.1538	+0.0538
At 21 C.						
95.5	95.25	—0.25	+0.1572	—0.0279	+0.1293	—0.1207
95.5	95.2	—0.30	+0.1571	—0.0279	+0.1292	—0.1708
95.3	95.15	—0.15	+0.1570	—0.0279	+0.1291	—0.0409
At 20 C						
95.3	95.15	—0.15	+0.1855	—0.0330	+0.1525	+0.0025
95.5	95.4	—0.10	+0.1862	—0.0330	+0.1532	+0.0532
95.3	95.2	—0.10	+0.1855	—0.0330	+0.1525	+0.0525
95.2	95.0	—0.20	+0.1856	—0.0330	+0.1526	—0.0476
					Average	—0.0247

[1] Paper presented at the meeting of the Association of Official Agricultural Chemists, Washington, November 22, 1911.

polariscopic degrees lower than the polarizations actually made at 20° C.

As the invert-sugar content of these sugars was not definitely known, a further investigation of 12 samples of raw sugar was made in which the invert-sugar content of each was accurately determined, giving the results shown in Table II.

By use of the formulas above given, the polarizations of all the raw sugars coming to two technical laboratories have been arranged in groups covering monthly periods, corrected for temperature and compared with the corresponding average polarizations obtained in the Sugar Trade Laboratory, when tested at 20° C.

TABLE II.

At 20°.	At 28°.	Diff	Calculated correction for sucrose alone.	Invert sugar.	Calculated correction for levulose alone.	Combined corrections.	Difference of calculated polarization from polarization at 20°.
95.25	95.1	—0.15	+0.2282	1.33	—0.0432	+0.1850	+0.0350
86.80	85.7	—0.10	+0.2057	2.50	—0.0812	+0.1245	+0.0245
94.25	94.0	—0.25	+0.2256	1.45	—0.0471	+0.1785	—0.0715
94.3	94.1	—0.20	+0.2258	1.39	—0.0451	+0.1807	—0.0193
	At 25°						
93.5	93.3	—0.20	+0.1400	1.84	—0.0374	+0.1026	—0.0974
94.7	94.55	—0.15	+0.1418	0.81	—0.0164	+0.1254	—0.0246
85.8	85.7	—0.10	+0.1286	1.77	—0.0359	+0.0927	—0.0073
94.7	94.6	—0.10	+0.1419	1.07	—0.0217	+0.1202	+0.0202
94.6	94.4	—0.20	+0.1416	1.45	—0.0294	+0.1122	—0.0878
	At 27°						
87.6	87.6	—0.00	+0.1839	2.15	—0.0595	+0.1244	+0.1244*
95.3	95.15	—0.15	+0.2001	0.91	—0.0260	+0.1741	+0.0241
94.6	94.4	—0.20	+0.1998	1.48	—0.0421	+0.1577	—0.0423
						Average	—0.0101
						Average without* =	—0.0205

Having applied the formulas for correction of sucrose and levulose, the results obtained in the last column show the differences of the polarizations made at high temperatures and calculated back to 20°, from the polarizations actually made at 20°. The average of 12 such determinations gives us a result for the sugars polarized above 20° of only 0.0273 polariscopic degrees lower than the polarizations actually made at 20° C. If we omit the tenth sample in the above series, which seems to be irregular, we find that the average calculated polarization is only 0.0186 polariscopic degrees lower than the polarization actually made at 20°.

These observations are quite in accord with those made by Browne, on mixtures containing known amounts of sucrose and levulose in raw sugars and molasses and reported by him in the article above cited.

The results found are expressed in the following table, which gives in decimal fractions of a single degree polariscopic the variations of my laboratory "A" and laboratory "B" results after calculating to 20° C., from the results obtained in the Sugar Trade Laboratory when conducting the whole operation at 20° C.

Thus we see that the average discrepancy in this series of about one thousand samples is only +0.0148 polariscopic degree, but that if the levulose correction has not been applied this quantity would be increased to +0.0499.

The levulose correction is thus twice as great as the total experimental error and should by no means be ignored. The ideal method is, of course, to conduct the entire operation of polarizing sugars at 20°, but as this requires an expensive plant or somewhat increased work and time by the method outlined

	Laboratory "A".				Laboratory "B."			
Date. 1911.	Sucrose cor.	Levulose cor.	Total cor.	Diff. from Trade Lab.	Sucrose cor.	Levulose cor.	Total cor.	Diff. from Trade Lab.
March	+0.0800	—0.0140	+0.0660	—0.0070	+0.0424	—0.0059	+0.0365	—0.0096
April	+0.1290	—0.0236	+0.1054	+0.0140	+0.0239	—0.0036	+0.0203	+0.0200
May	+0.2002	—0.0303	+0.1699	+0.1190	+0.0990	—0.0180	+0.0810	+0.0710
June	+0.1977	—0.0575	+0.1402	+0.0436	+0.1832	—0.0355	+0.1477	+0.0117
July	+0.2235	—0.0576	+0.1659	+0.0273	+0.2373	—0.0580	+0.1793	—0.0170
Aug.	+0.2329	—0.0634	+0.1695	+0.0625	+0.1177	—0.0344	+0.0833	+0.0193
Sept.	+0.1379	—0.0373	+0.1006	+0.0047	+0.1666	—0.0520	+0.1146	—0.0267
Average corrections for both laboratories			+0.1486	—0.0351			+0.1135	+0.0148

In order to get a further comparison between polarizations made at 20° C., and those made at higher temperatures, and calculated to 20° C., I have made monthly comparisons between the polarizations of many hundreds of samples tested both at the Sugar Trade Laboratory and at other laboratories.

above, cases will arise where a temperature correction will be required. My contention is that if any such correction is to be applied it should be done in accord with a full appreciation of the significance of levulose as well as of sucrose and thus be made as correct as our present knowledge will allow.

LABORATORY AND PLANT.

AN ELECTRIC LABORATORY FURNACE.

By Raymond C. Benner.

Received August 16, 1911.

In taking up the subject of methods of ignition, we must, of necessity, go back to the time of Bunsen. He would feel quite at home in this field, for, here, things have been at a standstill and we have remained about where he left us until within the last year or so, since which time more attention has been given to this important subject. In most places the Bunsen burner and air blast furnish the sole sources of heat for ignition purposes.

In order that a given compound may have a definite and constant composition for weighing, both the manner and temperature of ignition must be taken into consideration. In the case of many elements such as silicon and calcium, the form in which they are usually weighed is not altered by the highest temperatures obtainable with the Bunsen burner or the laboratory blast lamp. For such as these, this method of ignition may be used with perfect satisfaction.

Another factor, however, to be reckoned with, is the loss of weight undergone by the platinum crucibles when ignited in the open flame. By heating a platinum crucible weighing about 15 grams by means of gas, which contained considerable sulphur, the author has found this loss to be as high as 1 mg. per hour.

The question of temperature is likely to be the one of most importance, and one in which the analyst is most likely to err, since the various texts give but an idefinite idea as to the maximum temperature which certain precipitates will stand before undergoing decomposition, or, on the other hand, as to what temperature it is necessary to use in order to obtain a compound of definite composition. Treadwell's "Analytical Chemistry," N. Y., 1910, p. 167, says, in regard to the ignition of cadmium sulphate in a double crucible: "The outer crucible can be heated to the full red heat of the Teclu burner without running risk of decomposing the cadmium sulphate. It is, however, not necessary to heat it so strongly." In regard to the ignition of manganese sulphate, the following statement is found in Fresenius, *"Quantitative Analysis"*, N. Y., 1896, p. 158: "It resists a very faint red heat, but upon exposure to a more or less intense red heat, it suffers decomposition."

Electricity makes the most convenient, cleanest way of obtaining heat for many laboratory purposes, but when platinum resistance furnaces are utilized, the likelihood of their burning out, as well as first cost, often makes their use prohibitive. With the advance in the study of alloys, it has been found that an alloy of nickel and chromium, called "Nichrome," possesses properties which make it an ideal wire for laboratory resistance furnaces for temperatures up to a maximum of 1100° C. This alloy which melts at about 2800° F. is not easily corroded by ordinary laboratory fumes and has a resistance of about 68 times that of copper. This high resistance makes it possible to use electricity at 110 to 220 volts with very little, if any, external resistance in the circuit. This renders possible the construction of small laboratory furnaces for temperatures up to 1000° C. or 1100° C., not only at low cost, but with the additional advantage of economical operation because of the utilization of the currents ordinarily at hand. The furnaces most largely

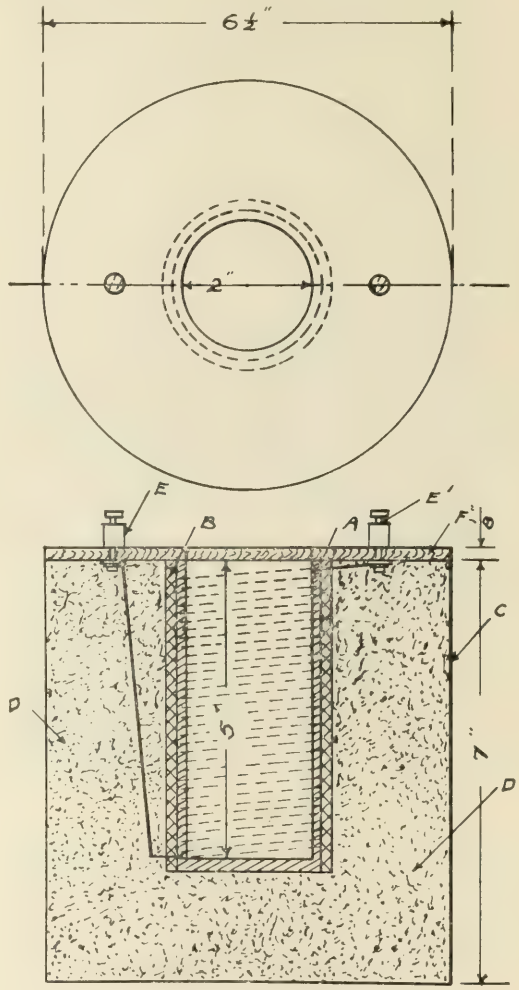


Fig. 1.

employed by us are of two types, but being made in the same general way, a detailed description of one will suffice. Somewhat similar combustion and treating furnaces have been described by Berry.[1] The furnace shown in Fig. 1 has for a foundation a small clay cup, such as is used in batteries. In the case of this furnace, it is $2^1/_2$" in diameter and 5" long, which size

[1] This Journal, 2, No. 6.

is very convenient for individual use. When resting on end it has been used for making fusions and when resting on the side, for ignitions. This furnace can be made to hold four crucibles at a time by inserting a long piece of asbestos board to form a bottom. Around the clay cup A is wound the "Nichrome" wire, the size and length of which may be easily determined, when the size of the clay cup and the voltage of the current to be used are known. One half the carrying capacity of the air-cooled wire, as allowed by the manufacturers in their bulletin (this can be obtained on request), should not be exceeded when the wire is enclosed in heat-insulating material, as we describe. In order that the furnace may not be readily burned out, wire of such size and length should be used for each furnace that it will be impossible to exceed one-half the carrying capacity of the wire when there is no resistance in the circuit. It must be remembered that a temperature of 1000° C. within the furnace means that the temperature of the wire carrying the current is much higher. After determining the length of wire with which the furnace is to be wound,

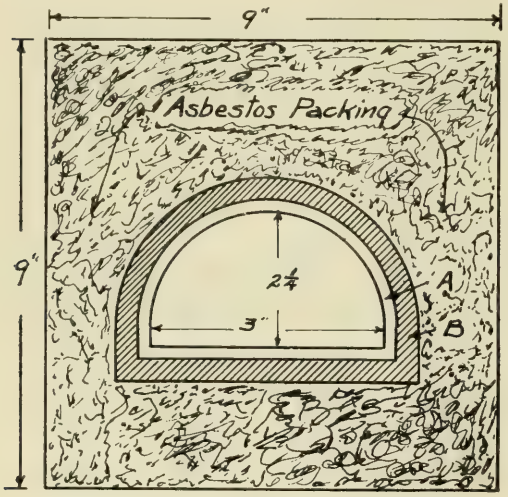


Fig 2

the winding may be commenced at the closed end of the muffle A (Fig. 1), enough free end being left to reach the binding post E. The wire is fastened by several turns of nickel or "Nichrome" wire of a larger size than that used in winding the furnace. The wire on the outer end of the furnace is wound a little close in order that the temperature may be equalized where radiation is greater. Great care should be used to avoid kinking the wire, as this renders it brittle. When the winding is complete, the end is fastened in the same manner as before, leaving enough free end to reach the binding post E'.

After the winding has been properly executed, the problem of proper insulation and protection from the air is to be considered. The insulation in itself is not difficult, but to find a material which will insulate, at the same time have no chemical action on the wires and yet protect them from the air at 1000° C., is more or less of a problem. Of the mixtures which have already been tested, the one consisting of one part kaolin to three parts of ground quartz gives the best results. The kaolin and crushed quartz are mixed to a paste with water and plastered over the wire and cup, care being taken to fill all

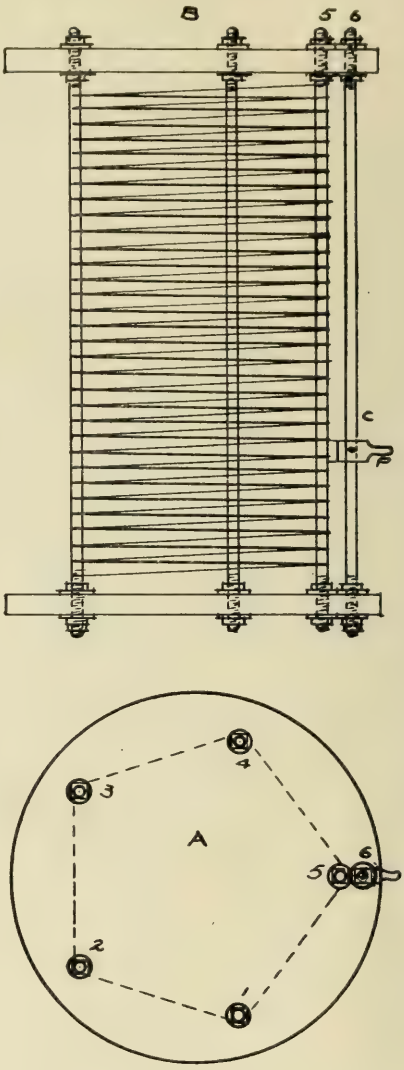


Fig. 3

space between the wires B (Fig. 1). This mixture is plastered on just thick enough to completely cover the wires. (If the coating is too thick it is likely to crack badly.) After drying and baking by means of the current, any imperfections are repaired and the baking repeated. This can be somewhat improved by painting with a dilute solution of water glass.

Now the furnace is ready for packing in the heat

insulating material D. This is done as shown in Fig. 1. The whole is then covered with a heavy piece of asbestos board F, and the binding posts E are placed as shown.

A furnace of the muffle type (Fig. 2) has likewise been constructed on the same general principles and has been found to be equally economical, as well as much more satisfactory when a large number of ignitions are to be made. This furnace is $10^1/_2$" long over all, while the muffle is $5^1/_2$" in length. The furnace is wired with No. 17 B. S. "Nichrome" wire. The same temperatures can be obtained in this furnace as in the one first described, but more care must be taken because of its increased size.

Without external resistance the highest temperature, to which it is safe to heat the furnaces, can be obtained when the furnace door is closed. Furnaces, constructed on the above plan and of the dimensions shown in the figures, as a rule, fulfil these conditions. Nevertheless the highest temperature obtainable in each furnace should be determined and not allowed to exceed 1000° to 1100° C., if the life of the furnace is to be considered. In order that a constant temperature less than the maximum may be obtained, it is necessary to have external resistance. A very convenient resistance box, shown in Fig. 3, can be made by using six stove bolts of $^1/_4$" iron, about 12" long, threaded at both ends, each end being provided with two washers and two nuts. The ends of the resistance box may be made of either asbestos board or wood, wood being the more satisfactory for boxes, which are to be used for small currents which produce but small amounts of heat. For boxes which are to be wound with heavier wire and used for large currents, which develop sufficient heat to warp boards, asbestos, although not as stiff, is more satisfactory. The five iron rods, 1 to 5 (Fig. 3), should be wrapped with thin asbestos paper which has been painted with water glass solution. The water glass cements the paper firmly to the iron, so that no trouble will be experienced with its peeling off. Bolt 6 is left bare. When the water glass is dry, the bolts should be fastened in position on the boards as indicated by 1 to 6 in Fig. 3.

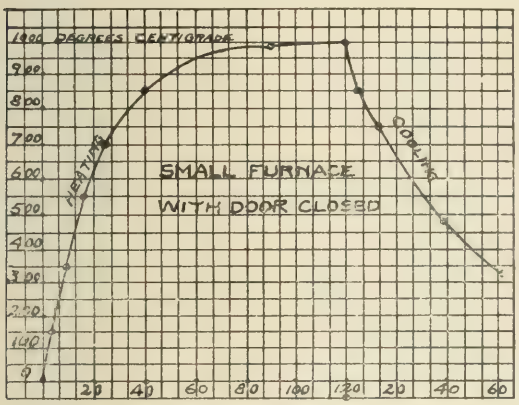


Fig 4

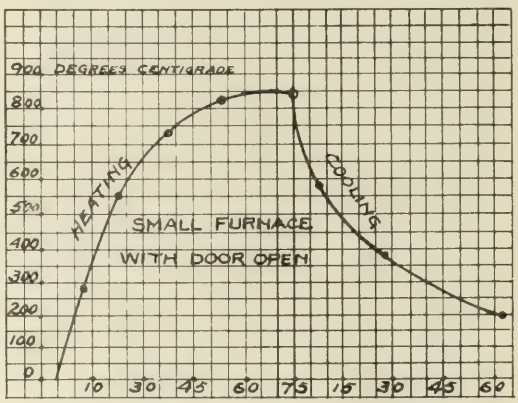


Fig 5

The slide contact is made of hard wood, the hole in the center being lined with copper by means of which contact is secured with the sheet of brass or "Nichrome" ribbon. The metal is kept in contact with rod 6, which passes through the metal lined hole, by means of a small screw. The brass or "Nichrome" sheet has enough spring to make a satisfactory contact, when pressed against the wire, where it winds about 5 by rotating around 6. This arrangement is quite satisfactory for currents up to 3 amperes, but for higher currents better contact is necessary and can be obtained by a thumb screw so arranged as to pass through C and press X against the resistance wire (Fig. 6).

When cleanliness and convenience are considered, there is no comparison between the electric furnace and gas as a means of making ignitions.

The first cost of the two furnaces as well as the resistance box can be seen from the following tables:

MUFFLE FURNACE.

Muffle	0.50
Wire 65 ft. No. 17 B. S. "Nichrome"	1.27
Labor at 50 cents an hour	1.00
Clay and quartz sand	0.10
Heat-insulating material (old pipe covering)	0.00
	$2.87

CRUCIBLE FURNACE.

Clay cup $2^1/_2$" × $4^3/_4$"	0.20
Wire No. 20 B. S. 32 ft. "Nichrome"	0.35
Labor at 50 cents an hour	0.75
Clay and quartz sand	0.05
	$1.35

RESISTANCE BOX.

Stove bolts	1.00
Wire 75 ft. No. 22 B. S. "Nichrome" with a resistance of about 70 ohms and a carrying capacity of about 6 amperes	0.80
Labor at 50 cents an hour	2.00
	$3.80

The cost of operation is as reasonable as the first cost. When used on a 110-volt circuit, with electricity at 10 cents per kw. hour, the muffle furnace, which takes 5 amperes, can be operated at a cost of 5 cents per hour and the crucible furnace, which takes 3 amperes, will cost 3 cents per hour. At the University

of Arizona, where gas is $1.50 per 1000 cu. ft., it costs about 1.5 cents per hour to run a Bunsen burner. Therefore, when, as is the rule, several ignitions are to be made, the electricity is considerably cheaper than gas since 2 to 4 crucibles can be ignited in the smaller furnace and 4 to 8 in the large. In these electric furnaces, temperatures can also be reached in a porcelain crucible which are rather difficult to obtain by means of a Bunsen burner or blast lamp.

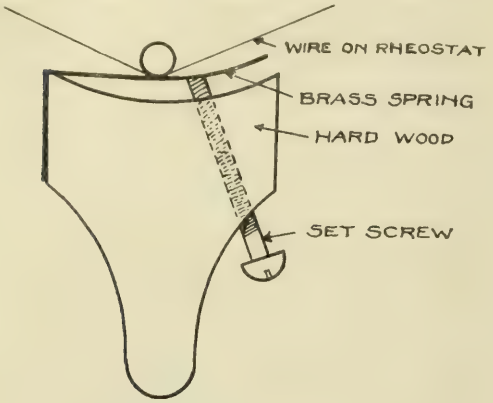


Fig 6

The heating and cooling curves (Figs. 4 and 5), taken with the door closed and open, show the rate at which the furnace will heat up and cool down. With ordinary usage, furnaces, made as described above, have a life of several hundred working hours and when one burns out it is only a matter of the expenditure of a few moments of time to renew the heating element.

UNIVERSITY OF ARIZONA,
TUCSON.

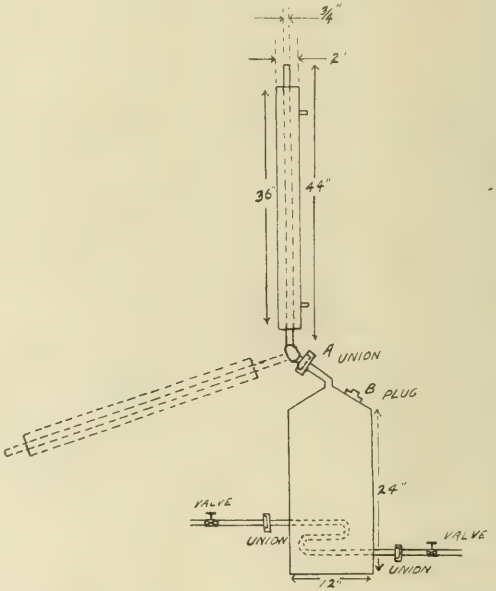
A STILL FOR ABSOLUTE ALCOHOL.[1]

By RALPH H. MCKEE.

Received October 17, 1911.

In a laboratory, in which considerable organic work is carried on, the expense of absolute alcohol in a year's time is a distinct item. The still shown in the accompanying sketch has proven efficient in the preparation of absolute alcohol from ordinary 94 per cent. alcohol. It is made of sheet copper tinned on one side, with a half-inch bent brass pipe (32 inches within the still. A greater length would probably be an improvement), whose upper end is connected with the main carrying steam at about 40 pounds pressure and the lower end with the same steam trap used for our still for distilled water. An opening, B, four inches in diameter, is used for filling and emptying the still. It is closed by use of the top of a plumber's drum trap such as is commonly used in connection with bath tubs. The still was made and installed by a local tinner at a cost of $21.00, not including the steam trap.

In operation the still is charged with 35 pounds lump lime and 26 liters of ordinary 94 to 95 per cent. alcohol. A current of water is started through the condenser and steam turned on until the alcohol has been heated to boiling and then turned off. This takes about five minutes' time and the dehydration of the alcohol once started evolves sufficient heat to keep the still hot some hours. To insure the completion of the dehydration, the steam is turned on the next morning and the heating with the condenser vertical continued for six or seven hours. The union A is then loosened, the condenser turned down into the nearly horizontal position shown in the sketch,



the union tightened and the distillation and collection of the absolute alcohol begun. At this point it is necessary to wrap some kind of a blanket about the body of the still, otherwise, owing to air cooling, the distillation will be slow and incomplete. To clean, the unions are opened and the still removed to a convenient place and washed out by use of a hose inserted into the four-inch opening B.

The yield is somewhat over sixteen liters of alcohol of slightly better grade (99.8 per cent.) than shown by freshly opened bottles of "absolute alcohol" from two well-known German chemical houses. The cost of the product is about $0.30 a kilo as compared with the ordinary purchase price of $1.10 a kilo, both being on the "duty-free" basis granted to educational institutions. Laboratories which cannot avail themselves of "duty-free" straight alcohol may find it worth while to prepare, by this apparatus, water-free alcohol from the ordinary denatured article.

UNIVERSITY OF MAINE,
ORONO.

[1] Another form of alcohol still is described by Warren, *J. Am. Chem. Soc.*, **32**, 698 (1910).

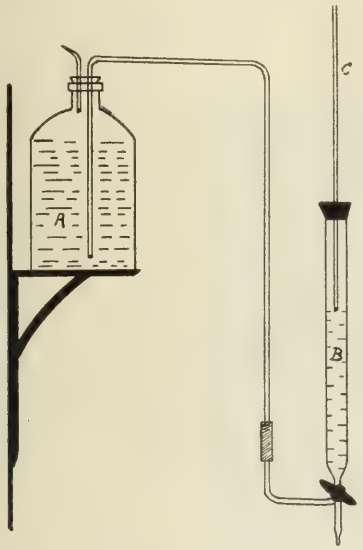
AN AUTOMATIC PIPETTE.

By T. O. Smith.

Received November 15, 1911.

Every chemist engaged either in routine work or in research involving a considerable number of determinations has learned to appreciate the value of any automatic or labor-saving device he may find available.

The automatic pipette here described is offered because of its simplicity, accuracy, ready adaptability to any volume required, and especially, because it is easily set up from materials and apparatus found in every laboratory.



The only materials needed are:

A—A bottle of a size adapted to the reagent which it is to contain.

B—A three-way stopcock burette.

C—A fine capillary tube long enough to reach from the zero reading on the burette to the top of the solution in the container.

D—Glass and rubber tubing to set up as shown in the illustration.

By raising or lowering the capillary tube *C*, the pipette may be adjusted to deliver any exact quantity within the limits of the capacity of the burette used.

It is obvious that if the capillary tube is drawn out as fine as possible and the burette and container brought near the same level, the accuracy of the pipette is practically that of the burette.

New Hampshire Agricultural Experiment Station,
Durham.

A NEW MELTING-POINT APPARATUS.

By D. S. Pratt.

Received October 26, 1911.

In the course of some research work with organic compounds, it became necessary to have a melting-point apparatus more accurate and more easily controlled than those ordinarily used. With all common types, the chief difficulty is in obtaining a uniform rise in temperature, and in duplicating the conditions at another time. The following simple piece of apparatus needs little explanation beyond the illustration. It is based upon the Thiele tube, with electricity supplanting the Bunsen flame, as heating agent. The lower half of the side arm is wound with resistance wire, such as fine manganin or nichrome. The whole arm is then enclosed with asbestos paste as shown in the cut. Using a lamp board, or rheostat, the current sent through the heating coil may be varied at will, and thus the rise of temperature very accurately controlled. By calibrating the instrument in terms of lamps and temperature it is only necessary to turn on the proper number of lamps and the rise of temperature will be exactly uniform each time it is used. The rate of change may be varied from an almost imperceptible rise, to a very rapid one, and the range is limited only by the fluid used.

In making a series of determinations it is very convenient to turn off, say, one lamp, while preparing the tubes, thus retaining the temperature within a few degrees of the melting point and saving much time usually spent in needless delay. For substances whose melting points vary with the rate at which they are heated, this device is especially convenient. It has been in use for over a year in the organic research laboratories of Cornell University, has given complete satisfaction and has supplanted the older types.

Cornell University,
Ithaca, N. Y.

ADDRESSES.

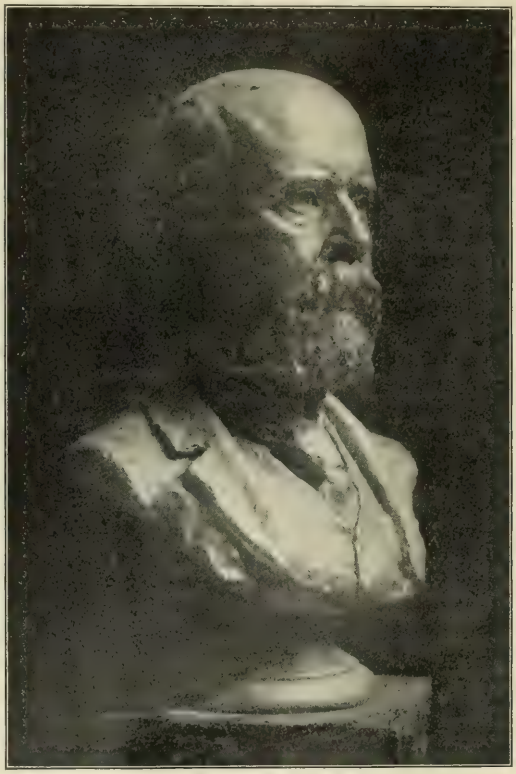
ADDRESS AT THE UNVEILING OF THE BUST OF WOLCOTT GIBBS.[1]

By Charles E. Munroe.

Received November 29, 1911.

[The unveiling of the Bust of Professor Wolcott Gibbs took place in Rumford Hall, Chemists' Building, New York City, on November 25th. The Bust was executed by Ernest Wise Keyser, and it will be appropriately placed in Rumford Hall among likenesses of other distinguished investigators in the field of chemistry.

The presentation address was made by Mr. Alfred Gibbs, representing the relatives and descendants of Professor Gibbs, and a review of his life work and history was given by Professor Charles E. Munroe.—Editor.]



Because of the place of his birth and that where he was educated; because of the profession he chose and which he so highly adorned; because during the greater part of his mature life he applied his splendid talents and broad attainments to the realization of the hopes of the founder of the Royal Institution in his bequests to Harvard College and to the American Academy of Arts and Sciences; and because he was an academician and a club man, it is eminently fitting that the bust of Wolcott Gibbs should be unveiled in the Rumford Hall of the Chemists' Club of the City of New York.

For on February 21, 1822, he was born in this city of New York; in 1841 he received his baccalaureate degree from Columbia College of this city; in 1845 he received the degree of M.D. from the College of Physicians and Surgeons of this city; he chose chemistry as his profession; he was Rumford Professor of Harvard College and Harvard University for 45 years and a member of the Rumford Committee of the American Academy of Arts and Sciences for 30 years; he was founder, member and president of the National Academy of Sciences; he suggested and organized the Union League Club of New York and he promoted and supported other social organizations.

His education was, however, much broader and more comprehensive than that comprised in his satisfaction of the requirements for the degrees awarded him at Columbia College and the College of Physicians and Surgeons, for in the interim between his graduation from the first-named institution and his entrance on the second he served as laboratory assistant to Dr. Robert Hare, Professor of Chemistry in the University of Pennsylvania, then the most eminent chemist America had produced and to-day revered for his splendid contributions to science. On his graduation from the College of Physicians and Surgeons, Gibbs went to Europe where, until 1848, he continued his studies under the direction of the eminent chemists, Rammelsberg, Heinrich Rose, Liebig, Laurent, Dumas and Regnault, whose names are each inscribed upon the honor roll of those to whom the chemistry of to-day owes its place among the sciences.

Broadened by travel, by contact with these eminent investigators, and the students that gathered about them, Gibbs returned to his native country for service in his profession, and found his first opportunity in the delivery of a short course of lectures in a minor institution in Delaware, but very shortly after, in 1849, he was appointed professor of chemistry in the Free Academy, now the College of the City of New York, where he remained until 1863 when he accepted the Rumford professorship, requiring service in chemistry, in the Scientific School of Harvard College.

His term of service in New York was distinguished, for, while his duty to the college demanded only that he teach its students the elements of chemistry, he began in 1851 as associate editor of the *American Journal of Science*, the preparation of abstracts of foreign literature in chemistry, and he engaged in research with the result that in 1857, there was given to the world the first memoir on a notable and systematic research in chemistry from America when the Smithsonian Institution published the memoir of Gibbs and Genth on "The Ammonio-Cobalt Bases" which has ever since served as a model for the pres-

[1] Delivered in Rumford Hall, Chemists' Club, New York, November 25, 1911.

entation of results by investigators in chemistry. In 1861 his independent paper on the platinum metals appeared and, as Clarke says, "firmly established his reputation."

Gibbs was in New York when our Civil War came on and devoted as he was to his profession he was also a patriot. It will be recalled that in broadly fitting himself for his profession he had at the College of Physicians and Surgeons pursued that branch of applied chemistry styled medicine and qualified in it, hence he could serve his country best and most by the exercise of his special knowledge and attainments. When men are rushing to expose themselves as targets for the enemy it requires a high degree of courage to offer on the altar of one's country one's special talents in service outside the firing line. But this Gibbs did and the U. S. Sanitary Commission stands to-day as an epoch in the civilization of man. By its work it proved, perhaps, to be the greatest good for mankind that was realized from that dreadful period of labor in which a great nation was born. It has been a model for other nations that have subsequently, unfortunately, been engaged in war.

Not content with applying his acquired knowledge, especially in that branch of applied chemistry known as medicine, to the amelioration of the "horrors of war" and to the aid of those that conquered, Gibbs sought to organize and crystallize opinion and effort by bringing together those of influence in New York who favored active military operations against the seceders and thus the Union League Club, which met, to organize, in his home, was formed. And throughout his life he was an organizer, or member, of bodies of men through which, by investigation, consideration, and discussion, issues of moment in science were carefully wrought out, while social relations were conserved and promoted.

He was born and reared under conditions that could have bred an aristocrat. His father was in affluent circumstances. His progenitors had served their country and mankind in positions of importance. He inherited a competency. His associations from earliest youth were with the cultivated, intellectual and forceful. He was in person impressive and engaging. He was in taste and dress discriminating; but he was in his dealings with and estimates of man democratic.

As a prospective student I met him in 1868 and he looked to me god-like. It was my good fortune not only to be received as a student by him but later to become his assistant, and through other fortunate circumstances, such as being ordered to duty in Newport, where he resided after his retirement, to keep in contact with him quite up to the time of his death. I recall most vividly my first meeting with him for he embodied in the flesh all that I had ever imagined of man and though my relations with him were afterwards quite close this feeling and belief persisted and remains. He was above the average man in height, and his body was symmetrically developed with his stature so that he walked and moved with natural gracefulness. His head was admirably proportioned and was covered with a splendid mass of curling black hair which matched the beard that covered his face. In clothing and person he was always decently fastidious, but ever the attracting features were his eyes, which were deep brown in color, lustrous and luminous; and his voice, which was full and rich, with a deliciously attractive and convincing overtone.

He gave the impression of mildness and fairness and continued association confirmed this first impression. Never have I met one who so avoided definitely judging his fellowman or who when forced to do so judged him more fairly and without prejudice, for his mind was filled with the contemplation of nature in a large way and of its processes, and he was endeavoring constantly to comprehend them and to record the results of his observations and tests for the benefit and use of mankind. He regarded his fellowman in the same broad and tolerant manner. In fact the definite impression of him which one received by close contact with him was largeness of vision; breadth of view; tolerance of differences in opinions, methods or manners; and sympathy, in a broad way, for mankind; and that he approached every issue, scientific or social, without prejudice, and with an entirely open mind.

If, in my attempt to portray Dr. Wolcott Gibbs from the image that abides with me, I have conveyed to you the impression that, through timidity or indolence, he sought to avoid strife, let me hasten to immediately correct this erroneous impression, for on the contrary he was intensely human and he met his troubles in a thoroughly human way but even then on a high plane.

Permit me to illustrate by an anecdote or two. Self-government by students is regarded in this country as a very modern and novel development. Dr. Gibbs introduced it at the outset of his coming to Cambridge. I do not know that he had not previously done so in the College of the City of New York. Eventually in my career as a student in his laboratory I succeeded to the first place in the governing body and I wore the resounding title of Chief of Police. During my administration a rebellion arose. The orders I gave were not obeyed and the fines I assessed were not paid. Having exhausted all the resources of authority at my command and the disorder having become a menace to all earnest students, after due warning, I resorted to the unheard-of expedient of reporting the recalcitrants to Dr. Gibbs. They were much amused when they were directed to report to this mild-mannered, sweet-tempered gentleman. I was not present at the interview. I never knew what occurred at that interview. The students never told me and Dr. Gibbs never referred to it. But what I do know is that when these students returned they said: "Munroe, you may order us to do what you wish; you may assess such fines as you please; but never again direct us to report to Dr. Gibbs;" and from that day until I left the laboratory discipline was complete.

Strange as it may seem Dr. Gibbs became, on com-

ing to Harvard, a storm center. President Hill called him because he had a vacant chair in chemistry to fill and he found in Gibbs the most eminent chemist in America. Gibbs accepted the position at Harvard because it seemed to offer the largest opportunity for usefulness in the field for which he was especially equipped. But his appointment thwarted the realization of the ambitions of others; it became a cause of dissension and the arraying of groups of men against each other. The situation had become acute as I entered upon the scene. In the regular performance of my duties I was unwittingly forced to know of it though then I knew not the reason for it or the extent of it. I was especially embarrassed to come upon Professors Gibbs and Cooke, when they were engaged in a gentlemanly, but very personal, altercation.

Unknowingly to me, out of this came my opportunity. While holding the position of private assistant to Dr. Gibbs I was appointed Assistant in Chemistry in the College under Professor Cooke. With the courtesy that prevails among gentlemen all these arrangements were ostensibly in the hands of Dr. Gibbs and it was from him that I received my instructions to make that visit to President Eliot at which I received notification of my appointment to the college. Naturally and most properly I reported to Dr. Gibbs that I had obeyed his instructions, and the results of so doing, and I can never forget his admonition. Knowing my loyalty to him, knowing that inadvertently I had become somewhat acquainted with the distressing situation he said: "Mr. Munroe I have been deposed and you are appointed to take my place. You know that my relations with Professor Cooke have not been entirely amicable, yet let me say that you can serve me best by serving him with entire devotion." Thus spoke the man in Wolcott Gibbs.

Were there time I should like to describe the laboratory at the Lawrence Scientific School and the manner in which it was directed by Dr. Gibbs. Fortunately this has been well recorded by Professor F. W. Clarke in his memorial Lecture before the Chemical Society of Great Britain and by Stephen Paschall Sharples in his description of the Lawrence Scientific School to the Cambridge Historical Society. I may say that were it to be investigated by an agent of the Carnegie Foundation, armed with a pad and pencil, it must have been condemned. I must further say that after completing my fortieth consecutive year of university teaching I should, if put under oath, state that, measured by pedagogical standards, it was unsound. But I must add that the results produced were splendid and that the students that survived the process went forth finely equipped to pursue their chosen professions. Dr. Gibbs' visits to us were infrequent but the impression he made in these conferences were such that he was an ever-living presence and a constantly present example. Mendenhall's remark that a student would prefer to be neglected by Rowland to being taught by another embodies the thought I desire to convey concerning the relation of Wolcott Gibbs as a teacher to his students. The pedagogue trains his pupils as the military sergeant drills the cowherd. But the educator educes from his student his best capacities in the line of his endeavor. He brings the within without. He reveals to the student the latter's own capacities. He preserves to the community that precious gift, individuality, but arouses, and enlivens, and controls it so that it may best serve the community in which that individual may be placed. It is impossible to formulate the manner in which this may be accomplished for the possibilities vary with each student to be taught and with him who teaches, and the teachers who comprehend this are rare, but such was Wolcott Gibbs.

It is said of Gibbs that he was not a "popular lecturer." I may say that this was most unfortunate for the populace. It has been my privilege to listen to a large number of those public speakers who have commended themselves to the public. As a youth I reported at length, for the newspapers, the lectures of Tyndall and Proctor. I served as demonstrator for Professor Cooke in that charming course of lectures at the Lowell Institute which appeared as "The New Chemistry." I sat at the feet of Edward Everett, Henry Ward Beecher, Wendell Phillips and Emerson. I was enthralled by Julia Ward Howe and Mary A. Livermore. Dr. Gibbs gave us but few lectures, but those were enriched by such a wealth of knowledge, graced with such diction, planned in so thoroughly logical and systematic a manner, and presented with such charming simplicity as to ever remain as almost unapproachable models.

For Dr. Gibbs was ever true to his best capacity (his proper sphere of usefulness to his fellows); namely research, and he continued this long after his retirement from the field of teaching. As one reviews his achievements in research one is amazed at the catholicity of his accomplishments. All recognize his numerous contributions to analytical chemistry; his application of the electric current to quantitative determinations being especially well known; but he covered the field from gravimetric, through volumetric, to gas analysis. It is also pretty generally known that his early investigations of the complex ammonium bases, and their compounds, were in his later life supplemented by researches into the constitutions of the complex inorganic acids. Organic chemistry claimed his attention. In 1853 he prepared an arsenical derivative of valeric acid. In 1868 he discussed the constitution of uric acid and its derivatives. In 1869 he described some products formed by the action of alkali nitrites upon them. In 1891 and 1892, with H. A. Hare and E. T. Reichert, he treated of the physiological action of definitely related chemical compounds. He produced memoirs on a normal map of the solar spectrum and on the wave lengths of the elementary spectral lines, and, in the study of interference phenomena, he discovered a constant, which he styled the interferential constant. The time allotted me is too brief to enable me to set forth the work of an investigator who at the age of

18 published a paper entitled a "Description of a New Form of Magneto-Electric Machine, and an Account of a Carbon Battery of Considerable Energy" and at 71 years of age published a method for the separation of the rare earths, further than to say that while Gibbs was an experimentalist rather than a theorist he published views on theoretical chemistry that have force to-day.

By virtue of his sympathy and breadth he became a pioneer in comprehending, assimilating and expounding the results of others, giving them always full credit. He was the first American to adopt and promulgate the conclusions of Cannizzario; so early as 1880 he appreciated the value of the researches of J. Willard Gibbs and was the prime factor in having the Rumford medal conferred on this immortal Yale physicist. I well remember his enthusiasm in those early days when speaking of the recently published, and now classic, memoir by Kekulé.

I fear the privilege you have afforded me to speak of my beloved master has tempted me to overstay the time allotted me and yet I feel I have but inadequately set forth the man and his achievements. In closing, permit me to quote from the admirable tribute paid him by Theodore W. Richards.

"The circumstances of his early academic life brought him in contact with but few students. This is the more to be regretted because his enthusiastic spirit, his tireless energy, his recognition of everything good, and best of all his warm human friendship which endeared him to all who knew him. Those who were thus fortunate, whether students or colleagues, will always devotedly treasure his memory; and his place as a pioneer in science in America will always be secure."

WOLCOTT GIBBS.[1]

Although I am unable to be present at the unveiling of the bust of Dr. Gibbs, I cannot let the occasion pass without some expression of my admiration for him; and in thinking the matter over, I have been struck with the contrast between his work and that of some of his followers in the study of the metal ammonia compounds, who seem to think that the main object of a research consists in providing oneself with a sufficiently flexible theory, and then fitting graphic formulas of the compounds to it with little or no attempt at experimental proof. Such researches, in which the pen is mightier than the test tube, had no attraction for Wolcott Gibbs. With him the test tube was supreme—in fact not only were his racks always full, but on his desk were many large beakers crowded with test tubes, each with a label sticking out of its mouth; and I remember few things so delightful and illuminating as seeing him flitting from one to another, dilating on the beauty of the crystals or precipitate, and pointing out its relation to past work and promise for the future.

In his obituary of van't Hoff, Emil Fischer said most good chemists follow their noses in research. This was eminently true of Wolcott Gibbs, and his scent was fine enough to guide him unerringly through the most intricate trails, for the hardest subjects had a special attraction for him.

Few chemists have been his equal in the power of appreciating the suggestiveness of observations, of contriving new and varied conditions for experiment, and in shaping imagination.

His work, however, was exclusively experimental. In fact some of us wished that he would have drawn more inferences from his discoveries, but I think that he considered that his real function was that of the experimental pioneer; and certainly he converted many a tangled almost impenetrable thicket into a pleasant grassy path between well-trimmed shrubberies.

CHARLES LORING JACKSON.

HARVARD UNIVERSITY,
November 22, 1911.

[1] Letter from Professor Jackson. Read at Unveiling of Gibbs' Bust.

CHEMICAL INDUSTRIES IN SWEDEN.

By THOMAS H. NORTON.

Sweden is a land in which chemistry has played an important rôle from a comparative early date. Scheele and Berzelius were among the most noted pioneers in the formative period of the science, and no less than 20 of the known chemical elements have been discovered by Swedes. The Kingdom owes to three factors its past and present position in technical chemistry. The first is a fairly abundant and diversified mineral wealth. Swedish iron and copper once dominated the world's markets. While no longer leading in quantity, Sweden still occupies a foremost position with regard to the quality of its metal products, and the high technical standard of its mining and metallurgical equipment.

A second feature is the enormous extent of the country's forests. Once contributing the necessary charcoal for its choice product of iron, they now furnish the raw material for an enormous industry—the manufacture of cellulose in its varied forms.

The third factor is Sweden's abundant water power. The coal deposits of the land are unfortunately limited and of inferior quality. The annual output is 305,000 long tons. In earlier days the forests supplied fuel. Now that timber possesses a greater value, and the supply is more limited, it has been necessary to import coal from abroad to the extent of 3,000,000 tons annually.

With the advent of electric power and its economical transmission it has been possible to utilize the waterfalls on a most extensive scale. Electrotechnical industries have promptly availed themselves of this opportunity. The total available water power of the Kingdom is estimated at over 4,000,000 horse power. About one-ninth has thus far been harnessed for industrial purposes. Each year at present there is an additional increase of over 100,000 horse power. In 1911 it is estimated that this increase will be about 115,000 horse power. Owing largely to this rapid exploitation of her vast water power, Sweden is changing from a producer of raw materials to a predominantly

[1] Special report to U. S. Consular Service.

manufacturing land. Modern industrialism is rapidly invading every field of national activity.

The chemical industry of the country is confined chiefly to inorganic branches. Apart from the wood pulp, and the products of the electrochemical branches, it is in most cases inadequate to meet the demands of the home market of a population of 5,500,000. It is, however, expanding steadily, more rapidly than the growth of population.

According to the census of 1900 there were 256 chemical factories, employing 2,644 workmen, with annual products valued at $4,095,000. To these should be added 187 factories producing oils, tar, etc., with 2,434 workmen, and an output of $5,650,000, and the match industry with 20 factories, 6,102 workmen, and products valued at $2,665,000. Paper and allied branches were credited with 159 factories, 18,490 workmen, and an output of $8,130,000. The metallurgical industries give employment to 16,876 workmen, and the products are valued at $49,050,000. For purposes of comparison the statistics of other leading industries are here given: Mining, 13,187 workmen, output $5,430,000; metals and machines, 56,222 workmen, output $44,840,000; textiles, 37,187 workmen, output $36,100,000.

The 256 establishments classified by the census as chemical works are subdivided as follows:

Character of products.	Factories.	Workmen.	Value of products.
Inorganic acids, bases, and salts	32	291	$ 683,000
Fertilizers	72	921	1,402,000
Explosives	19	664	897,000
Colors and miscellaneous	133	768	1,113,000

For its supplies of most heavy chemicals Sweden is still to a great degree dependent upon other European countries.

Sulphuric acid is made largely in connection with the manufacture of superphosphate. In 7 factories, with 39 workmen, there was an annual output of 35,108 metric tons (metric ton = 2,204.6 pounds). Twenty years before the output was but 4,000 tons. The output nearly covers the domestic demand. Pyrites is used chiefly in the works, and is imported from Norway and Spain. There is also a considerable consumption of Sicilian sulphur.

There is but one factory for caustic soda and bleaching-powder. Both articles are imported chiefly, as is also the case with soda and its various by-products and derivatives. In the list of salts, however, there is one notable exception in the case of potassium chlorate. This compound, so important in the domestic match industry and in the maufacture of explosives, is now one of the leading staple products of Sweden and is extensively exported. The electrolytic process by which it is produced was devised in 1893 by Director O. Carlson, who started the first electrochemical establishment in Sweden. In 1900 the two factories employed 215 workmen, and the chlorate produced was valued at $214,000. In 1909 imports of chlorate had sunk to 207 tons, and the Swedish factories were not only meeting the home demand but exporting annually 1,400 tons to other countries. The industry uses potassium chloride from Stassfurt as its raw material.

Carlson's method is an advance upon preceding processes for the electrolysis of alkaline chlorides, as he does not use diaphragms in the electrolytic bath and maintains a continuous operation. Cathodes of iron are employed, but the anodes, which were originally of carbon, are now of platinum-iridium gauze. Formerly the baths were kept slightly alkaline by additions of caustic potash or lime. Now they are kept slightly acid, as free hypochlorous acid favors the formation of chlorate. Small amounts of potassium bichromate are also added to prevent the reduction on the cathode of the potassium hypochlorite primarily formed. The process is noteworthy as the sole important instance where an electrolytic method has proved to be economically superior to an old, established process of chemical manufacture and has effectually displaced it. In Germany only one factory has tried to maintain its manufacture of potassium chlorate by the old process, using Deacon Chlorine. In England the old process is likewise being gradually abandoned.

FERTILIZERS.

Agriculture is highly developed in Sweden, one-half of the population being engaged in tilling the soil, and the demand for artificial fertilizers is extensive. Although there are large amounts of apatite in the country, it is impossible to compete with the raw phosphate brought from Florida, Algiers, and the Pacific. About 29,000 tons of Chile saltpeter are imported annually. Thomas slag is worked up very advantageously, as some of the Swedish iron ores are very rich in apatite and yield with the basic Bessemer process a very rich slag. Three factories grind this slag, producing 10,000 tons annually. As the demand for Thomas iron is limited, the production will not increase materially.

A few years ago Prof. Wiborgh devised a method for utilizing the phosphoric acid in the Swedish iron ores, which carry especially large amounts of apatite. These ores are finely ground and the resultant powder submitted to the action of powerful magnets. By this means the apatite is largely freed from the iron oxide. It is then fused with soda and the phosphoric acid is brought into the citrate-soluble form of tetracalcium phosphate. The product compares favorably with Thomas slag and even superphosphate in fertilizing efficiency. A factory was started at Svarton to manufacture the so-called Wiborgh phosphate, but after a short period the works were closed.

There are numerous factories for producing bone meal, as well as bone fat and glue and animal charcoal, and a few establishments for making poudrette. Herring guano is a staple article. At Gothenburg and its vicinity there are 17 factories engaged in extracting herring oil and preparing the residual press cakes for fertilizer. The annual product is valued at $285,000, of which $208,000 is represented by the

guano. This industry depends on the success of the annual herring catch.

In 1900 Sweden consumed 253,132 metric tons of artificial fertilizers, of which one-half were produced at home. In the course of a decade the industry has developed so rapidly that there is now a surplus of superphosphate available for export, amounting to 17,000 tons in 1909.

EXPLOSIVES.

The manufacture of explosives constitutes one of the leading industries of Sweden, largely owing to the genius and inventive ability of Nobel. In addition to dynamite his other leading invention, ballistite, a smokeless gunpowder consisting of a gelatinized mixture of nitroglycerin and guncotton, is manufactured. Originally the Nobel Co. prepared this powder from equal parts of the two constituents. It is now made from one part nitroglycerin and three parts guncotton. A small amount of diphenylamine is often added. Gelatinization is effected by means of a mixture of alcohol and ether (2 to 1).

Another distinctively Swedish explosive, Lamm's bellite, is manufactured to a limited extent. Its base is dinitrobenzene, and it belongs to the class of picrate powders. The growth of this branch of manufacture in Sweden has been remarkable. In 1870 there was one factory, employing 40 workmen, with an annual output of $34,000. In 1900 there were 11 factories, with 394 workmen, and an output of $724,000.

COLORING MATTERS—CARBIDE AND VANADIUM SALTS.

Small establishments manufacturing coloring matters produce pigments of domestic materials, lampblack, ochers, zinc white, white lead, and cobalt blue, and prepare also, for use in solution or composition, the different organic dyestuffs, imported chiefly from Germany. There are 46 factories, employing 130 workmen, producing wares of an annual value of $234,000.

Acetylene is widely used in Sweden, and the carbide industry was founded almost as early as in the United States. Two factories, one at Alby and the other at Trollhattan, with a total of 5,000 horse power, produce not only enough for the needs of the domestic market, but also export annually about 1,600 tons. The actual cost of production is given as 3 cents per pound.

Sweden has in the past supplied the world's demand for vanadium compounds, vanadium chloride for the aniline-black dyeing, and ammonium vanadate for use in steel-making. The exportation is now much less than formerly, for aniline black and copper sulphate and sulphide are more in use now as catalytic agents.

MATCHES.

The match industry is one of the most important in the Kingdom and has grown rapidly. Twenty factories produced matches valued at $3,422,000 in 1909. Nine-tenths of the total product is exported. These Swedish matches are encountered all over the world, despite a very keen competition. The export interests complain of the high protective duties in most countries. In France, Spain, and Greece matches are a Government monopoly.

The Swedish factory equipment contains many devices for replacing manual labor. Lagerman's "complete machine," introduced in 1892 at the Jonkoping works, is one of the most ingenious labor-saving devices known. The match splints, already cut into the proper form by other appliances, are fed regularly into one end of this machine and emerge at the other end a finished product, packed in boxes ready for shipment. One such machine produces hourly 3,600 boxes of matches.

Aspen wood is used almost exclusively in the match industry. It is easy to cut and porous enough to admit easily of impregnation with sulphur or paraffin. The domestic supply of aspen of good quality is now seriously reduced, and much is imported from Finland and Russia. Most of the chemicals used—phosphorus, antimony, sulphur, and paraffin—are imported. This was also formerly the case with potassium chlorate until the recent establishment of the Swedish electrolytic manufacture. In 1901 the Swedish Government forbade the sale in the Kingdom of matches made with yellow phosphorus. At present the manufacture of the old-fashioned matches is much less than formerly, although the Jonkoping works produce a considerable quantity in which yellow phosphorus is replaced by innocuous phosphorus sesquisulphide. In manufacturing the standard safety matches of Sweden now the splints are first soaked in paraffin, or in a concentrated solution of ammonium phosphate. The ignition mass for the heads consists of potassium chlorate, mixed with sulphur or antimony sulphide, gum, or dextrin in solution, and small amounts of powdered glass and ferric oxide. Potassium dichromate and manganese dioxide are occasionally added as oxidizers. The friction surface on the boxes is coated with a mixture of red phosphorus, antimony sulphide, and dextrin solution.

The largest factories in the Kingdom are the two at Jonkoping and the "Vulcan" at Tidaholm. Under their lead nearly all the other manufacturers have combined to prevent undue competition and facilitate the export trade. This latter is carried on largely through Hamburg and London, which serve as distributing points for much of the world's trade in matches. There has been a rapid shrinkage of the export of Swedish matches to Germany, partly as a result of recent legislation. In 1909 the export was 1,655 tons, and in 1910 but 44 tons.

WOOD PULP.

The manufacture of cellulose, or wood pulp, is another highly developed Swedish industry, based also primarily upon its forest wealth. The factory for grinding wood, established at Trollhattan in 1857, was the pioneer of the pulp industry. The preparation of chemical wood pulp was introduced in 1871, the soda process being used. In 1874 came the sulphite process, Francke using calcium bisulphite, and

Ekman the magnesium compound. Both of these methods are now utilized, but that of Ekman is used to a less extent on account of its greater cost; the product is, however, of a remarkable purity and gloss, and it is preferred as raw material for the finer qualities of paper. Swedish wood pulp ranks high, as the wood employed—aspen and spruce—is freer from resin than that available in most countries. The pulp factories of Sweden number 122, and in 1900 employed 6,910 operatives and produced 417,000 metric tons of pulp.

The exports of pulp reached 564,000 tons in 1909, as against 229,000 tons in 1900, and consisted of 372,000 tons of dry chemical pulp, 31,000 tons of wet chemical pulp, 46,000 tons of dry mechanical pulp, and 115,000 tons of wet mechanical pulp. The total value of the exports was $15,372,000. Great Britain takes about 60 per cent. of the export, other heavy purchasers being France, Norway, Germany, Belgium, Denmark, and, recently, the United States.

There has been a serious overproduction of wood pulp during the past three years and prices have been much disorganized. Recently the wood-pulp associations of Sweden and Norway have agreed upon a systematic limitation of the production of mechanical pulp for 1911 and 1912. The prospective reduction during the period ending January 1, 1913, is fixed at 150,000 tons. No restriction is placed on the output of chemical pulp. As a result of this agreement prices of mechanical pulp have already been materially advanced.

PAPER.

The manufacture of paper is naturally closely allied with that of cellulose. In 1909 Sweden had 66 paper mills, employing 7,725 operatives, the production amounting to 250,000 tons, of which 137,510 tons, valued at $7,346,000, were exported. The ratio of increase is about the same as that of cellulose. Of the paper exported, 80 per cent. goes to Great Britain and is used chiefly for newspapers.

Swedish filter paper for chemical purposes has maintained a world-wide reputation for a century. For a long period it was regarded as indispensable for the needs of the analyst, and the manufacturers enjoyed a practical monopoly. Rivals in other countries, especially in Germany, now compete in furnishing a filter paper carefully freed by treatment with hydrochloric and hydrofluoric acids from mineral matter. The remarkable success attained in earlier years by the largest Swedish firm was due to the use of the purest water available for manufacturing purposes and the choice of exceptionally pure raw material. The peculiar properties of the paper were largely secured by freezing it while in a moist condition. The formation of ice crystals rendered the feltlike mass sufficiently porous for the purposes of rapid filtration. This Swedish firm manufactures now a very choice grade of writing paper, made by simply dipping its filter paper into sizing.

ALCOHOL—NEW SOURCE OF SUPPLY.

Another industry, that of the manufacture of alcohol, is now linked with the great cellulose interests. The customary methods of distillation are well developed in the country. There were in 1900 131 distilleries, producing annually 450,000 hectoliters (11,887,650 gallons) of spirits containing on an average 50 per cent. of alcohol. Much of this is for use as a beverage. Of the total amount 62 per cent. is manufactured from potatoes, 35 per cent. from maize and grain, and 3 per cent. from beets and molasses. There were 429 distilleries in 1875 and only 131 at the close of the century.

The chemists of Sweden have experimented in a variety of ways to solve the problem of manufacturing alcohol from wood and thus find an additional source of revenue from the country's forest wealth. In the production of wood pulp by the sulphite method there is a waste product that the chemists have finally been able to utilize with profit in the production of alcohol. The profitable utilization of the exhaust lyes drawn off from sulphite boilers has always been a problem. For every ton of cellulose made by this process there are 10 tons of these lyes. They contain one-half of the weight of the wood originally introduced into the boilers. Among the matters present are dextrose and various other sugars, xylose, acetic acid, tannic acid, nitrogen compounds, resins, etc., as well as the calcium lignin-sulphonate, the chief product of the reaction. Of the sugars present most are susceptible of fermentation. They constitute about 1 per cent. of the lyes. The treatment of the liquid is comparatively simple. It is first neutralized with calcium carbonate, after which yeast is introduced. When the fermentation is complete the alcohol produced is secured in the ordinary manner. The process yields 6 gallons of alcohol (100 per cent.) for 1,000 gallons of lye. About 14 gallons are secured for every short ton of cellulose.

As may be imagined, methyl alcohol and other volatile compounds are contained in this crude alcohol. It is sold and used as denatured alcohol for heating and technical purposes. The excise rates in Sweden have been adjusted so as to aid this new industry. If the process were extended to all Swedish sulphite works, the annual output would be about 3,500,000 gallons. It is doubtful whether a sufficient demand exists for this grade of alcohol to furnish a home market for such an amount. German chemists are skeptical as to the possibility of producing the alcohol economically under existing conditions in the Empire, where, on the basis of the Swedish results, over 8,000,000 gallons could be produced annually.

In the attempts to manufacture alcohol directly from wood, investigation so far has been directed to the simple reaction involved in combining one molecule of water with one molecule of cellulose, and thereby producing dextrose, from which alcohol is obtained by fermentation. Chemically, by treatment with sulphuric acid under pressure, this change can be readily effected. From ordinary wood, alcohol amounting to 5 or 6 per cent. of the original weight can be thus secured. Pure cellulose yields 15 per cent. The problem is essen-

tially of an economic nature. It is claimed in Sweden that it has been solved, and that a method has been elaborated for utilizing the waste of the sawmills. Details are not given.

DISTILLATION OF WOOD.

The distillation of wood developed at an early day in Sweden, as was to be expected in a land so rich in forests. Swedish tar was exported to every land and given the preference for coating vessels and their rigging, walls, roofs, and roofing paper. It continues to enjoy its good repute, but exports are less in quantity than was the case half a century ago. There has been renewed activity during the past decade. The foreign trade in this article shows the fluctuations: 1875, imports 1,700 and exports 8,300 metric tons; 1900, imports 1,700 and exports 3,600 metric tons; 1909, imports 200 and exports 7,614 metric tons.

The industry is now centered in the northern section of the Kingdom and shipments take place chiefly from the port of Umea. Much of the tar is produced in a small way in old-fashioned tar hollows by individuals or families. There are some more modern establishments, where iron retorts are installed. The census of 1900 reported products from such works valued at $58,000. As the exports alone of wood tar had a value of $135,000, it is evident that the bulk of the output comes from small producers. There are now about 25 firms engaged in the business, most of them carrying it on in connection with extensive lumbering and wood-pulp interests.

The Skogens Kolaktiebolag, at Kilafors, is the leading company devoted exclusively to wood distillation. It uses annually for this purpose over 100,000 cubic meters of pine wood (cubic meter = 35.314 cubic feet). A good example of the diversity of interests carried on by a Swedish company is seen in the case of the Stora Kopparbergs Bergslags Aktiebolag, of Falun. This company is said to be the oldest industrial corporation in the world, having received a royal charter in 1347 after a previous existence of over a century. For two centuries, prior to 1750, it was the chief producer of copper in the entire world. Since then, as the copper supply diminished, it has devoted itself to iron, and is to-day the leading producer of iron and steel in Sweden, owning the largest iron works in northern Europe. During the past century it gradually increased its land-holdings until it now owns 750,000 acres of forest and has become the largest exporter of forest products in the Kingdom. At Skutskar it operates what is thought to be the largest sawmill in the world, and at Kvarnsveden it lately built a combined pulp factory and paper mill at a cost of $760,000. Its annual dividends are 14 per cent.

The Kilafors Co. and a few others, notably the Skanaska Attikfabriken, of Perstorp, furnish a wide variety of products obtained from the destructive distillation of wood. Their lists contain the various charcoals, wood naphtha of 64°, methyl alcohol free from acetone, pyroligneous acid, technical and crystallized acetic acid, formaldehyde, creosote, carbonates of creosote and guaiacol, turpentine, lampblack tar oil, carbolineum (for the impregnation of wood) pitch, etc. Little effort is made to go further in the isolation of the numerous other constituents of wood tar, or to use those separated for the manufacture of higher derivatives.

Forty years ago factories were started in Sweden for the purpose of utilizing the stumps of spruce and other conifers, by subjecting them to destructive distillation. Apart from tar, etc., it was sought to secure more particularly the crude wood oil, used in place of turpentine. This branch of manufacture has not been very successful, as it has not been possible to free the product from a pronounced burnt odor. At present six small factories carry on this distillation. The production of resin and turpentine is strangely limited for a country so rich in conifers as Sweden. There is an annual import of 400 tons of turpentine.

PRODUCTION OF COAL TAR.

There are 27 gas works in Sweden, but with the abundant water power and cheap electricity the industry does not expand rapidly. At Gothenburg the annual per capita consumption is 1,236 cubic feet. At Stockholm it is 3,088 cubic feet. Ammonia is collected in a few works in the form of the sulphate. The tar from the larger works is used for producing asphalt, carbolic acid, and creosote oils, chiefly for impregnating wood. The domestic supply of tar is insufficient, and there is an annual import of about 2,800 metric tons. One reason for the limited production of coal tar is the fact that Sweden possesses no coking coals and is forced to import coke from abroad. But little is done to carry on any systematic separation of the constituents of coal tar, apart from the carbolic acid.

A Swedish firm has introduced a novel and valuable feature into the treatment of coal tar. The Aktiebolaget Joh. Ohlsson's TeckniskaFabrik, of Stockholm, has solved the problem of removing the carbon from coal tar. The black color of tar is due to the presence of a large amount of carbon in an extremely finely divided state. It constitutes about one-quarter of the weight of the crude material. As the liquid tar has about the same specific gravity as the solid carbon, the latter remains suspended. The firm in question has succeeded in completely isolating the carbon from the liquid constituents of tar, leaving the latter in the form of a clear, transparent, gold-brown liquid. Such a purified tar is evidently much better adapted for fractional distillation than the crude material, and should facilitate the separation of the hydrocarbons and other compounds with a high boiling point, an operation rendered difficult in the process of ordinary tar distillation, owing to the foaming caused by the fine carbon toward the end of the operation.

The carbon separated by the Ohlsson process is totally different from lampblack in its physical properties and is distinctly of a graphitic nature. When pressed into a compact form it furnishes admirable

electrodes for arc lighting and also for electrochemical work. It could probably be used with equal advantage in making crucibles, as it possesses marked superiority over retort graphite.

Details are withheld with regard to the method used for effecting the separation. In all probability light hydrocarbons are added to the tar to lower its specific gravity, and the actual separation is brought about by the use of centrifugals. The added hydrocarbons can be removed by distillation from the residual liquid tar. This process is worthy of careful study, owing to its possible bearing upon the isolation of the more complicated higher-boiling constituents of coal tar.

SUGAR.

Despite the northerly climate and various other unfavorable conditions, the production of beet sugar in Sweden has increased, until sugar importation has practically ceased. Beginning with 1 factory in 1876, there are now 20 in active operation, the largest producing 120 tons daily. The total annual production is about 130,000 tons. There are 9 sugar refineries employing 2,402 operatives. All factories employ the diffusion process. The industry is located entirely in the lower end of the peninsula. Seed is brought from other more favored lands. The average yield of sugar is very high, taking all factories into consideration, being 3.5 metric tons per hectare (2.47 acres). The average yield in France and Belgium is 3.2 tons and in Germany 4 tons. The industry has been fostered by a protective tariff, amounting at present to 1.82 cents per pound. The rate of duty has varied at different times, but has never been less than 1.6 cents. A helpful factor in establishing new factories has been the remission for five years of all taxes on such works when built at least 19 miles from any existing factory.

STARCH, GLUE, GELATIN AND YEAST.

Starch is manufactured on a somewhat extensive scale, chiefly from potatoes. There are 95 factories, producing a total of 7,580 tons annually. This meets the entire domestic demand. A large share of the product is changed into glucose and used for conserves. Glue and gelatin are likewise produced in nearly sufficient quantity to meet domestic needs. There are 13 factories, employing 223 workmen, and producing wares valued annually at $300,000. Yeast is made in several factories, the annual ouptut being 2,785 tons.

OILS.

In 1900 there were 14 oil factories, employing 159 operatives. The annual product was 11,736 tons of oil cake and 4,418 tons of linseed and rape oil, as well as small quantities of fish oil and train oil. In 1909 Sweden imported 16,904 tons of animal and vegetable oils, 872 tons of train oil, 684 tons of oleine, and 8,017 tons of fats.

One Swedish specialty in this branch deserves note. The "Collanoljefabriken" has produced for a number of years an oil very highly valued for treating leather and rendering it waterproof. The composition and manufacture are kept secret, but it is supposed to be extracted from certain tropical plants. The oil is extremely viscous, can be drawn out in long strings, and repels water to a most pronounced degree. As a leather preservative it seems to render exceptional service.

MISCELLANEOUS.

The soap industry is highly developed. There are 42 factories producing annually 13,000 tons of soft soap and 3,700 tons of hard soap. Excellent toilet soap is manufactured in a few establishments. Imports of soap are relatively small. In some factories the production of scents is also extensive, the annual output being valued at $200,000. This is about six times the value of the imports of scents.

The candle industry is so developed that it practically supplies the domestic demand. There are 3 factories, employing 312 workmen. The annual product, which includes also stearin, is valued at $6,188,000. The imports are insignificant.

The domestic demand for varnish is very nearly covered by Swedish works. They number 15 and employ 91 workmen.

The manufacture of cement has grown rapidly of late years and is now an exporting industry. In 6 works 1,336 operatives are employed. The annual output of 126,000 tons has a value of $1,130,000. About one-third of this is exported, chiefly to the adjacent countries.

There are Swedish concerns engaged in the manufacture of lactic acid, lanolin, fruit essences, cosmetics, and pharmaceutical preparations, and some of the last named are of international repute. Liquid carbonic acid is made in three factories, the total annual output being 415 tons.

MINING AND METALLURGY.

The mining and metallurgical interests are so closely connected with chemical industries that a few data are appended. In 1902 30,700 workmen were employed, of which 14,600 were employed in mining proper, including 10,500 in the iron mines.

The quantities of ores and minerals produced in 1902 were as follows, in metric tons: Iron ores, 2,897,000; lead and silver ores, 9,400; copper ores, 30,000; zinc ores, 49,000; manganese, 2,800; clays, 216,000; feldspar, 18,000; coal, 305,000. In 1908 the production of iron ore had increased to 4,713,000 metric tons, of which 3,444,000 were exported.

Metals were produced in 1908 as follows, in metric tons: Pig iron, 556,000; iron and steel bars, ingots, blooms, etc., 772,000; zinc, 274; lead, 277; copper, 2,807. Silver to the extent of 1,389 pounds and gold to the extent of 44 pounds were also produced.

Iron constitutes 95 per cent. of the value of the metallic output. Most of the companies engaged in the production of iron and steel are partners in the Järnkontoret, an association that represents

a peculiar valuable method of organization for mutual aid and protection.[1]

IMPORTATION OF CHEMICAL GOODS.

In the following table a detailed statement is given of the imports of chemicals, drugs, dyes, and raw material used in their manufacture, as furnished by the annual report of the Swedish customs administration for 1909.

Articles.	Metric tons.	Articles.	Metric tons.
Fats	8,017	Cosmetics	11
Oils, non-volatile	16,904	Perfumes	8
Petroleum	111,485	Soap:	
Train oil	872	Toilet	46
Camphor	14	Ordinary	260
Gums and resins	4,302	Albumen	3
Turpentine	412	Animal charcoal	186
Coal tar	2,782	Celluloid	22
Wood tar	200	Collodium	2
Barytes	529	Enamel material	102
Cryolite	57	Rennet extract	91
Fluorspar	672	Rubber, artificial	24
Magnesite	728	Varnishes	340
Pyrites	78,049	Medicines	137
Candles	46		
	COLORS, ETC.		
Alizarin	64	Lampblack	66
Annatto	11	Lithopone	960
Blacking	123	Paints	149
Bronze powder	8	Printers' ink:	
Bronze and chromium colors	110	Black	94
Catechu	207	Colored	22
Cinnabar	15	Quebracho wood	5,245
Coal-tar colors	687	Red lead	1,003
Colors in tubes and glass	13	Red ocher	542
Dyewoods	503	Sumach and extract	56
Gall apples	16	Tanning materials	6,286
Indigo:		White lead	510
Extract	37	Zinc, white	2,692
Synthetic	46	Other colors	2,563
	CHEMICALS.		
Alum:		Hydrochloric acid	2,134
Chrome	65	Iodine and iodides	4
Potassium	29	Lanolin	6
Alum cake	349	Lead acetate	61
Alumina	4	Lime	1,146
Aluminum sulphate	1,024	Lysol	1
Ammonia	13	Magnesium:	
Ammonium:		Chloride of	425
Carbonate of	137	Sulphate of	140
Chloride of	226	Naphthalene	74
Nitrate of	11	Nitric acid	89
Sulphate of	76	Nitric ether	5
Antimony	118	Nitrobenzene, mirban oil	46
Argols	19	Opium	1
Arsenic, white	13	Oxalic acid	38
Borax	365	Phosphorus	88
Bleaching-powder	3,018	Phosphoric acid	25
Boric acid	76	Potash, caustic:	
Bromine and bromides	10	Liquid	21
Carborundum	3	Solid	4
Cement	12,776	Potassium:	
Chloroform	6	Carbonate of	1,312
Citric acid	14	Chlorate of	207
Cobalt oxide	3	Chloride of	1,805
Copper sulphate (blue vitriol)	104	Chromate of	87
Ferrocyanides	11	Cyanide of	4
Ferrous sulphate (green vitriol)	945	Nitrate of	267
Formalin	5	Sulphate of	26
Glycerin	214	Sulphide of (incl. Na_2S)	451
Graphite	442	Quinine preparations	1.3
Saccharin	4	Sulphur:	
Salicylic acid	4	Crude	23,255
Salt:		Flowers	59
Crude	2,174	Refined	3,521
Refined	24,143	Sulphuric acid:	9
Soda, caustic:		Fuming	509
Solid	1,111	Ordinary	1,446
Liquid	8	Superphosphate	2,845
Soda ash	13,490	Tartaric acid	36
Sodium:		Thorium nitrate	1.7
Acetate of	36	Tin and lead oxides	58
Chlorate of	3	Tin salts	1
Chromate of	8	Water glass	405
Nitrate of	28,894	Zinc	8
Sulphite and hyposulphite of		Zinc chloride	50
Sulphate of	20,226	Other chemical preparations	1,444

[1] A report covering the workings of the Järnkontoret, or Iron Institute, and the progress it has made in the reduction of iron ore in electric blast furnaces was published in Daily Consular and Trade Reports for July 19, 1911.

It will be seen from the table that Sweden offers a fairly good market for a great variety of chemical products. Germany is the chief source of supply. The United States furnishes 78,143 tons of the petroleum, 4,314 tons of lubricating oils, 3,913 tons of molasses, 812 tons of fats, 1,157 tons of cottonseed oil, 1,543 tons of corn oil, and 284 tons of other oils.

EXPORTATION OF CHEMICAL GOODS.

In the following table are shown the Swedish exports in 1909 of chemicals and goods in the manufacture of which chemicals are used:

Articles.	Metric tons.	Articles.	Metric tons.
Fats	735	Wood pulp	564,000
Oils and olein	1,299	Ammonium sulphate	331
Coal tar	4,461	Calcium carbide	1,556
Wood tar	7,614	Cement	33,197
Turpentine, crude	191	Copper sulphate	182
Feldspar	16,575	Ferrocyanides	69
Rennet	61	Potassium chlorate	1,400
Soap	59	Sodium:	
Lampblack	392	Chlorate of	483
Red ocher	216	Sulphate of	598
Tanning extracts	196	Sulphuric acid	203
Matches (value, $3,050,000)	26,868	Superphosphate	17,245
Paper	137,510	Tin and lead oxides	60

THE FUTURE FOR SWEDISH PRODUCTS.

From the foregoing table it is evident that, apart from the magnificent array of its wares based upon wood as a primary material, Sweden has already begun to export in quantity several other products of its chemical industry. The chief representatives in this class are cement and superphosphate, supplied chiefly to adjacent countries, and the chlorates and calcium carbide, products of the recently established electrochemical works. It is likely that the exportation of the latter products will steadily expand and that Sweden will become a strong competitor in the world's markets for electrochemical products on account of the cheap water power. That its paper and pulp exports will continue to increase is likewise probable. While for the moment the match trade shows no evidence of a check, there is less confidence in its future growth. Tariffs, fiscal regulations, and an increasing power and efficiency among foreign competitors are threatening to restrict the field of operations very seriously. For the time being the

United Kingdom and the British Colonies are the best customers of the Swedish match trade.

EXPORTS TO THE UNITED STATES.

The values of the exports of chemical products to the United States in four years, 1907–1910, were as follows:

Articles.	1907.	1908.	1909.	1910.
Cement	$ 41,000	$ 7,000	.....	.....
Chemicals (chiefly caustic alkalies)	6,000	4,000	$ 7,000	$ 13,000
Fusel and tar oil	....	2,500	.....	5,400
Glue	....	3,000	.....	.....
Matches	112,000	124,000	207,000	157,000
Paper	276,000	496,000	850,000	623,000
Wood pulp:				
Chemical	....	.....	1,318,000	1,636,000
Mechanical	499,000	1,060,000	.....	4,500

The United States purchases Swedish bar iron to the amount of over $1,000,000 annually, and about $600,000 worth of wire rod, as well as smaller quantities of several other forms of the metal. The export of Swedish ferrosilicon to the United States was valued at $5,000 in 1909, while in 1910 it had attained a value of $51,000. Of much greater interest is the sudden increase of the American demand for Swedish iron ore. The value of the importations ranged from $12,000 to $32,000 during the period 1907–1909. In 1910 the figure reached $983,000. For a number of years past America has purchased Swedish pig iron to an average annual value of $90,000.

IMPORTANCE OF THE SWEDISH MARKET FOR CHEMICAL GOODS.

As the American manufacturers of heavy and finer chemicals approach the point of competing with Germany and Great Britain in the world's markets, they will find in the Swedish trade an important field. For the time being there is an opportunity to extend trade in colors, paints and pigments, blacking, varnishes, and a few similar articles, the value of which is already appreciated in Sweden. The consumption of quinine preparations is also relatively large.

The outcome of the Swedish studies in the electric smelting of iron ores may mean much for certain iron deposits in the United States where conditions are not unlike those existing in Sweden.

FUEL ECONOMY IN FACTORIES.[1]

By C. E. Lucke.

Received November 13, 1911.

Maximum economy in the use of fuel as one of the primary raw materials in manufacturing is to be measured by the least consumption per unit of manufactured product, a statement ridiculously easy to make but most difficult of realization. The difficulties in realization arise from the almost infinite variety of combinations in the uses to which the heat liberated by combustion may be put, and the relation of heat quantities entering into each of the different uses of the heat, the difficulty in measurement of heat quantities, and the bulkiness of the records of the heat balance required to keep track of the heat disposition in the establishment. No one would think for a moment, in conducting the financial operations of a business, of dispensing with records of expenditures and income or fail to provide a more or less elaborate cost system for distributing the expense over the various parts of the apparatus used in production and for dividing cost of the products into the different elements that make it up. No one would think of attempting to economically manufacture a steam engine without providing for a regular systematic determination of the cost of the crank-shaft and in some instances for the distribution of the cost into elements of raw steel from which it was made, the operations of forging, machining, transporting and handling, and for the fixing of the overhead charges, all of which are determinable items, and to which may be added many others of lesser importance, carrying the process as far as the information is worth. Cost information is worth as much as the possible saving in cost of production to which the information leads, so that manufacturing managers must use and do use their best judgment in deciding how far they will detail their cost records, but it will be difficult to find one who would attempt to carry on his business without cost records as elaborate as the conditions warranted. It is quite the same with fuel economy, that is, so far as need of records is concerned but by no means the same in practice. There can be no rational attempt made toward fuel economy in a given system of manufacture using fuel without a knowledge of the distribution of the heat of that fuel throughout the establishment, and it is no more difficult to trace the heat throughout a system supplied with heat than it is to trace expenses for material and labor in a crank-shaft or fly-wheel relating each to the total expense incurred. though it is quite possible that the information may not be worth enough to warrant as complete a distribution of the expense of heat supply or as elaborate a system of records as would be warranted in the case of labor or materials entering directly into the factory product. However, there can be no question as to the absolute necessity for some heat accounting to determine the coal heat charge to be attached to each individual process using heat and to show sources and quantities of utilizable waste heat, however simple the system of the accounting may be, nor can there be any doubt as to the increasing justification for more and more elaborate records as coal cost forms an increasing fraction of the total cost of production. How many factories there are in which no more records of heat are kept than the cost of coal per month is impossible to state in the absence of statistics, but according to my own observations the number will be very large, probably in excess of three-quarters of the total establishments. It is not surprising, therefore, that maximum heat economy is so seldom attained or that managers are so constantly besieged and bewildered by, and so much dependent upon, the statement of promoters of all sorts of schemes

[1] Address delivered at the joint meeting of the A. C. S., S. C. I and A. E. S., New York, November 10, 1911.

who promise to accomplish most impossible economies and yet whose absurd arguments cannot be answered because of absence of data. How many managers, having under their direction steam plants for power, know the cost of their draft sufficiently closely to be in a position to judge the value of a new draft system offered for their consideration? How many know even the cost of the power itself so as to be in a position to judge a new power system offered as a substitute? It is safe to say that those who have data of the above sort constantly up to date are far less in number than those who know the total cost of their product and its fractional part of overhead charges, labor and materials and yet every one will claim a desire for fuel economy.

Heat accounting is necessary. How much accounting depends upon the fraction of total production cost chargeable to fuel in one form or another and through these accounts economy may be affected most readily by attacking first the big losses or items of large heat waste. In this way and only in this way may the best results be obtained from a given installed system in operation or the relative value of a competing system judged, as a preliminary to a change of system. In many cases it will be found that managers believe they have records of their heat distribution and power cost but these figures are what their so-called operating engineer hands them. It is most curious how the engine room cost figures are so seldom subjected to critical analysis and checking to make sure that they include all the items that are properly chargeable to that account or to insure the correctness of the items that are reported. This is in striking contrast to the care with which so-called factory cost systems will be installed and operated by experts in the same establishment which is satisfied with the accounting of a skilled mechanic called an engineer for its power and heat cost.

Economy is then always a question of accounting, that is, correct accounting as elaborate as the conditions may warrant in every establishment. The attainment of maximum economy is, however, also largely a question of the operating system used. It is one thing to know for a given plant in operation where the heat losses are and how much they are; it is another thing to know how to reduce these losses in the existing system by modifying the detail of management or even altering connections or substituting new units, but it is quite a different thing to know when or how to change the system as a whole to an entirely different one or how to compare broadly existing with possible new systems.

In a general discussion of fuel economy, it seems as if the question of system ought to be put in the first place, especially if it can be shown that there is any fundamental and essential differences in the losses involved and hence in the net fuel economy of the system applied to a factory. It may be assumed that in a factory fuel enters directly or indirectly into four classes of services, all of which are essential to the making of the product:

1. Power.
2. Factory heating in cold weather.
3. Factory lighting.
4. Direct manufacturing processes, such as heating, cooling, evaporating, condensing, melting and drying.

In a given establishment the system involving all these processes may be self-contained or may be externally sustained. A system is self-contained when all four classes of service may be derived from the same coal supply. It is not self-contained when it is partly or wholly dependent upon external supplies as, for example, gas for lighting alone, electricity for lighting alone, or for power in addition, and perhaps for high temperature furnace work with coal for the other services. In all systems where coal is used in manufacturing, its heat is rarely applied directly to the service to which it is ultimately put, but its heat is usually transferred in part to steam or transformed in part to combustible gases, giving in the former case the steam system of heat distribution and in the second case the gas system. Where heat of coal is directly applied to such service as high temperature heat supply, that service can always be better done by gas derived from the coal in just about the same degree of gain in efficiency as in the gas over the coal-fired cook stove. There is one exception to this, however, and that is where fixed carbon enters as a necessary element in a thermal reaction, but these cases are so clearly exceptional as to need no comment.

The primary process in the use of heat is, therefore, the making of steam on the one hand, or the gasifying of coal on the other, and the direct loss encountered in either of these processes is the first factor for measurement and record in the heat-accounting system. This first step of conversion may be made to take place with an average efficiency of 65 per cent. to 75 per cent. for the steam system, depending on the coal, the goodness of the firing and the type of equipment, and an efficiency from 75 per cent. to 85 per cent. for the gas system, showing a clear gain of about 10 per cent. for the gas system on the average for this first step, with, however, a limitation and this limitation is the inability of the producer to handle as wide a range of fuel with equal success to that attainable in the boiler.

Steam once made is transmitted in pipes for short distances only and under high pressure with constant heat loss for every foot and involving high maintenance charges, on its way to engines for shaft power or electrical generation. The gas, however, may be transmitted at low pressure over very long distances to all the buildings of large establishments or to neighboring establishments several miles away or from a central gas generating station dozens of miles distant through pipes cheaper than those required for steam and with almost no maintenance cost in comparison. This pipe distribution cost is the next item in the accounting and without setting down numerical values is again plainly in favor of the gas system, which involves no heat loss whatsoever while the steam involves a large one and in which the pipe maintenance costs are hardly comparable at all.

The next step is the conversion into work, in the engine, of the heat carried by either the gas or the steam, and here the balance is again in favor of gas as the gas engine is a much more efficient heat converter than the steam engine in the small sizes found in the average factory and even in larger sizes also, though there to a lesser degree. Few factories would find any occasion to use engine units exceeding 1000 h. p., which size, operated condensing, whether of the turbine or compound Corliss sort, will yield thermal efficiencies less than 20 per cent., whereas, operated non-condensing, these efficiencies would drop to at least 15 per cent. A smaller steam engine of, say, 100 h. p., will be less efficient and the turbine would not be so good as the piston type, though the difference would not be so very great. For this size the efficiency that could be counted on would be about 15 per cent. operated condensing and not over 10 per cent. operated non-condensing. Compare these efficiencies with the sure and substantially constant thermal efficiency for the gas engine in all sizes, of 25 per cent., which indicates a margin in favor of the gas of at least 5 per cent. for large steam engines condensing, 10 per cent. for the smaller condensing and also for the large non-condensing and 15 per cent. for the small non-condensing steam engines. These efficiencies are not the best ever obtained but are about as good as one can count on obtaining in factory work. Of course, load fluctuations will affect the result but these figures are for a load equally favorable to the two classes of machines.

If electricity is generated and transmitted for lighting or for use in electric motors the efficiency of electrical generation, transmission and reconversion to power and light is the same for both systems. It is right here, however, that another item may be put on the credit side of the account in favor of gas and one that is not generally or sufficiently appreciated, arising from the possibility of eliminating some of the electrical equipment, if not all. If machines are to be driven in various distant parts of the establishment there is no reason why we should not do as has been done more often in Germany, and that is to set down small individual gas engines at the spot where power is required and transmit gas with practically no loss instead of generating electricity and transmitting it to electric motors with three losses. This would not only save the expense of the electrical equipment but would save all electrical losses, which are often considerable, especially when generator and motor work at unfavorable loads. This is a perfectly feasible proposition and will give substantially the same efficiency of conversion as is obtainable in a single large central engine, a fact that distinguishes the gas system more than anything else from the steam system. Concentration of many small steam engines into a single large one always results in steam economy, a fact which has led to constant concentration of steam systems into larger and larger central generating units, so that the steam may be regarded as a centralizing influence whereas, on the contrary, the constancy of gas engine efficiencies in large or small sizes must characterize the gas system as a decentralizing influence in the interests of economy.

Take next the question of factory lighting of the self-contained system, which may be electrical with current supplied by either steam- or gas-driven generators and which can be only electrical for steam engine-driven generators but which may be something else when gas is available. There is no good reason for assuming that mantle lights of fair brilliance and moderate gas consumption cannot be produced to operate on weak producer gas for factory lighting and as soon as they become available, as they surely will when the demand becomes pressing enough, mantle gas lighting with producer gas will displace to a very large extent electric lighting in those establishments where the gas system is used for power and heat and gas transmission substituted, at least in part for electric. This sort of change while not feasible now, because of the lack of development of weak gas, mantle lights, will add another credit item in favor of the complete gas system and the possible gain in fuel economy for lighting should be incentive enough to produce these lights and warrant their quite general use.

Heating of buildings is almost universally accomplished by means of steam- or water-heated radiating surfaces at a temperature of 200 degrees Fahrenheit or thereabouts and there is no good reason for changing the system. The preparation of this low-pressure steam or moderately hot water can be done with equal efficiency by either the gas or steam system in cold weather, though the latter again receives a credit charge for all the rest of the year when heat is not required. For example, if the exhaust steam from steam engines is used it must be at approximately atmospheric pressure to give a high enough temperature, or live steam must be used either alone or added through reducing valves as make-up. In any case the heat put into the heating system gives about 100 per cent. effect in the warming of buildings, especially when drips are returned. This is also the case for the gas system as jacket water heat and exhaust gas heat can be combined for the same purpose and fresh gas drawn upon through thermostatic gas burners to supply any deficiency. By either method the effect is the same, full use of waste heat and 100 per cent. efficiency in the use of fresh supplies of heat in the warming of the building. During the time of no building heat requirement, which in this locality lasts for more than half the year, the waste heat of the steam engine is far in excess of that of the gas engine, especially if the former be non-condensing as is usually the case where exhaust steam-heating systems are in use so that measured over the whole year the gas system is again most favored.

There remains now to examine the possibilities of credit or debit items for the two systems in applying the heat to the direct manufacturing processes, which may be for convenience divided into low temperature heating and high-temperature heating, the former including most of the evaporating and drying

processes and the latter roasting, baking, melting, etc. All low-temperature processes can be carried on by steam-jacketed chambers or steam coil apparatus, using live or exhaust steam, a fact that has led to the design and mechanical perfection of many appliances now regarded as standard and for which there is no gas-heated equivalent. There is no good reason, however, why equivalent apparatus should not be quite as effectively designed and with efficiencies over 90 per cent. for operation with gas burners but like the mantle light the need has not yet been strong enough to warrant their production. Such evaporators concentrators, cookers and driers as fall in this class will, when gas-heated, offer still further simplification of piping and reduction of piping loss over their steam-heated equivalents and should be equally effective. High-temperature heating can be accomplished only by oil, piped illuminating gas or independent coal fires with the steam factory system while the gas system offers a possibility of producer gas-fired furnaces for practically all services and with almost perfect temperature control better by far than is possible with oil or coal and more economical because excess air and incomplete combustion can both be eliminated.

Thus, for the heating processes of manufacture, the gas system offers the same high-temperature source of heat, a gas fire, for all, while the steam system requires fresh fuel for the high temperatures, accomplishing the low-temperature service with live or exhaust steam, but the former is not an accomplished fact simply because no one is yet prepared to sell gas-fired appliances to take the place of steam-heated ones.

Comparing gas and steam systems broadly by summarizing the preceding brief analysis, it appears that the self-contained factory plant may be much more economically operated by the former than by the latter for all the services of power, lighting, building and process heating, but this is not all, for there is also in favor of the gas a very great simplicity in the heat balance determination for the gas over the steam so very great as to make it easier to keep up the operating economy nearer to the high possibility by quick and easy determination of wastes. For example, by means of a central gas meter and as many individual distributing meters as the separate consumptions of gas, the gas generated may be easily known as well as its distribution throughout the plant for all purposes by no more complicated procedure than the reading of meter dials which any good boy can do. Add to this recording calorimeters, and gas meter readings can be reduced by one multiplication to heat consumed by each part of the system. With such a ready check on consumptions and losses, it is sure that heat-accounting will be practiced because the cost of the account will be so small and, therefore, the plant may be and will be operated at somewhere near its good economy point. This is in most striking contrast to the case of the steam system where the possible economy is not only less but where in addition the realized economy is so much below its own maximum possibility simply because of the difficulty of making the measurements necessary to a heat balance with reasonable accounting costs. In the first place it is impossible to continuously measure the heat supplied in steam generated because there is no reliable and cheap steam meter available and even if there were, the heat equivalent of a pound of steam constantly varies with feed temperature, steam pressure and its wetness or superheat. Pipe line losses can be determined only by collecting and weighing drips; steam consumptions of other appliances and their heat equivalents is a question of many recording steam meters, steam calorimeters, thermometers, pressure gauges and automatic water weighers. To keep up all the instruments of this sort that would be needed so that they will remain reasonably accurate and to make the calculations of combining the various readings to get a heat balance would in most cases cost more than the information would be worth though a partial record is always a paying thing when designed to include the big items.

Why is it then, in view of both the higher possible economies of the self-contained gas factory system for the four classes of factory service and the correspondingly easier and cheaper fuel-accounting that would follow its use, that there is to be found no such system in use? The answer is as complex as a detailed study of the systems, but a few facts stand out more prominently than others: First, there must be put the inertia of the human mind, which resists the mental effort necessary to bring about a change when things seem to be running fairly well in the older way. There is always a latent suspicion that the new thing may not work however clear a case is made out for it on paper, and even if the manager himself is convinced in the light of his trained ability for clear independent thought, he may not be able to convince his board of directors who are ordinarily incapable of thinking in terms of anything but past performances of the factory, however willing they may be to deal in the futures of stocks and bonds. So far there has been in this particular case some good reason for suspicion, not of the scientific engineering possibilities but of the business expediency of a general change because of the lack of standardization or mechanical perfection of some of the needed appliances. We have no producer gas mantles for lighting, no gas-fired evaporators, concentrators or driers, and most important of all, we have no universal gas producer capable of economically using any available solid fuel, but it is for us to make these things, and my main object in speaking on this subject is to stimulate their production by showing a motive. Let the gas appliance makers get to work on the problem of adapting apparatus for all the manifold services of lighting and heating to the use of weak producer gas and let us all, chemists and engineers, try to solve the gas producer problem. Progress in the perfection of appliances for using producer gas will stimulate the demand for the right sort of gas producer to generate it, and the appearance of the producer on the market will force

the creation of gas-burning industrial apparatus so that each reacts on the other. As soon as the industrial world concerned with fuel economy in manufacturing demands these things in a sufficiently strong and positive manner they will be produced.

DEFLOCCULATION.[1]

By Edward G. Acheson.

Received November 18, 1911.

It is with much diffidence that I come before you to speak on a subject that has not yet emerged from the embryonic state. My latest experimental researches had to do with it; I believe it will rapidly grow in importance in the scientific industrial world; and finally much work of a strictly scientific character remains to be done to reduce the fragmentary knowledge we now have of it to an exact science.

In my labors devoted to working out and developing industrial and commercial projects, I have upon several occasions found reactions, conditions and results that did not harmonize with the accepted theories and formulae of scientific men. Being an earnest believer in publicity, in order that any possible benefits that might accrue to the common welfare may the more quickly be enjoyed, I shall lay before you a detailed account of my experiments on the deflocculation of inorganic bodies. It will become very evident, as my story unfolds, that throughout the series of experiments described and the working hypothesis employed, I was wholly disregarding the prevailing theories, and that I unconsciously entered the field of colloids.

Having worked out the problems involved in the manufacture of graphite from coal and other carbonaceous materials, I undertook, in the summer of 1901, the introduction of this artificially made graphite into the crucible trade. My first efforts were devoted to the making of a satisfactory crucible of my graphite, using as a binding material American clays. Many failures were met with, and I found it difficult to locate the cause of the failure, whether with the graphite or with the clay. I soon learned that the manufacturers of crucibles in the United States invariably used, as a binding agent for the graphite in the crucible body, clays imported from Europe. I secured samples of these imported clays, and found them much superior to the American ones in plasticity and tensile strength.

Chemical analysis failed to disclose the cause of the physical differences existing in the clays. The question involved interested me greatly, and I decided to endeavor to determine what produced the variations. I found it generally stated in the books that residual clays were non-plastic, and sedimentary clays were more or less plastic. Here was the starting point. Plasticity was developed by or during the act of transportation from the point of formation to the final resting place of the clay. I did not believe there was anything in the simple act of the suspension in water that would produce the effect noted, and therefore looked for the cause of the foreign matter carried by the water. It seemed that the most likely agents were the organic substances washed from the forests into the running waters. With this idea in view, I made a few experiments with those substances I thought likely to be found in the washings of vegetation. One of my early experiments was to treat kaolin with a solution of tannin, and I at once noticed less water was needed to produce a given degree of fluidity; also that the tensile strength and plasticity were increased.

"Tests were made on the increased tensile strength of clay, as the result of treatment with organic matter, and it was found that briquettes made of Harris kaolin and dried at 120° C. would break with a load of 5.73 kilograms per square centimeter, while the same clay, after treatment with 2 per cent. of catechu for a period of ten days, then formed into briquettes and dried at 120° C., would not break until the load was increased to 19.75 kilograms per square centimeter—an increase of more than 244 per cent.

I now began to wonder whether or not the effect I had discovered was known, as it might have much value to an industry of such colossal dimensions and antiquity as clay-working. Moreover, it would be amazing if it should not be known, in view of the tremendous amount of experimental work that had been done on that art. I searched for some record of the addition of organic matter to clay during its working, and only one instance could I find, that of the Egyptians in brick-making, as recorded in the fifth chapter of Exodus. The accepted theory of using straw fiber as a mechanical binding agent had never appealed to me. Straw, however, contains no tannin, and the effect I had found had always been produced with tannin, or a substance containing tannin. I procured some straw, boiled it with water, decanted the resultant reddish brown liquid, and mixed it with clay. The result was like that produced with tannin, and equal to the best I had obtained. It now seemed likely that the Egyptians were familiar with the effect I had discovered, and believing this was why they used straw in making brick and were successful in substituting stubble for the straw, I called clay so treated "Egyptianized Clay."

The effect of organic matter, as typified by tannin, in producing deflocculation and a resultant colloidal state of clay is very readily shown; for instance, I have here some powdered kaolin, a small quantity of which I will place in a test tube, add water, and after shaking, set aside. Another portion of the kaolin I will put into a beaker, and moisten with a water solution of tannin, to which a small amount of ammonia has been added. After a thorough mixture has been made, using a glass rod to stir with, to eliminate as much as possible any grinding action, I will add more water and divide the contents of the beaker between two test tubes. To one of the tubes containing tannin-treated clay I will add a little common table salt. The three tubes I will place here before you, that we may examine them later.

[1] Address delivered before the Society of Chemical Industry, London, November 7, 1911.

In the Summer of 1906 I succeeded in making artificially a high-grade graphite which I wished to make applicable to all kinds of lubrication. To meet the various demands, it would be necessary to have it remain diffused in liquids lighter than itself; for instance, water and petroleum oils. Recalling the effect of tannin on clay, which caused it to remain diffused in water, I treated a sample of my graphite with tannin, and found the same effect occurred. The graphite being black, it makes a better lecture demonstration than the clay I have shown you, and I will repeat my experiments, using graphite. I have here a sample of artificially made graphite, which has been disintegrated to a fineness that will permit it to pass through a sieve having 40,000 meshes to the square inch. I will introduce a small quantity of it into a test tube, add water and, after shaking, set aside. Another sample I will place in a beaker and moisten with a solution of organic matter, and after thoroughly stirring with a glass rod, I will add water and divide it between two test tubes, to one of which I will add table salt. These three tubes I will place beside those holding the clay, to be examined later.

The actual amount of deflocculating effect produced on the graphite in the beaker is very small indeed. In commercial work considerable mastication and time are required. I have here a bottle containing water having two- to three-tenths of 1 per cent. of its weight in deflocculated graphite; the deflocculation having been produced by a treatment similar to that I have applied to the graphite in the beaker, and a little of it being poured on a filter, you see the black liquid running into the test tube below the filter. The paper retained none of the graphite on its upper surface, all of it having passed into and through the paper. I will now add two or three drops of acid to the black liquid in the tube, and after warming over a spirit lamp, will throw it on another filter paper, and you now see a clear, colorless liquid descending into the tube below the filter. This is the water in which the graphite in a deflocculated condition was diffused; the graphite having been flocculated by the acid is now retained on the upper surface of the filter paper. The effect I have produced with the acid could have been produced with a solution of salt, lime water, or any one of that large list of substances known as electrolytes, even so weak an acid as carbonic acid if caused to bubble up through water carrying deflocculated graphite will cause flocculation and sedimentation.

Upon being deflocculated, the graphite is diffused through the water in a colloidal state, and I have samples of deflocculated graphite in water which have stood for more than two years without showing any settling, notwithstanding the graphite is two and two-tenths times heavier than water.

I have been able to obtain this same effect on natural graphite, amorphous alumina and silica, lampblack, and my manufactured product—Siloxicon, which is an amorphous body having the formula Si_2C_2O. The effect can be produced with a long list of organic bodies; for instance, tannin or organic substances containing tannin, also with solutions containing the gum of the peach and cherry tree, or extracts from straw and grass. The off-fall from the barnyard proved to be very efficient. I speak of these organic substances as agents when used to produce deflocculation, and they act as protective colloids to the deflocculated body.

Some minutes have now passed by, and we will examine the tubes containing the clay and the graphite. We find the clay that had been mixed with plain water has settled. The mixture of clay, water, organic matter and salt has also cleared, while the tube containing the clay, water and organic matter remains muddy. In like manner the tube containing the disintegrated graphite in water has cleared; the second one containing water, graphite and organic matter remains black; while the third tube, which was set up the same as the second, but had a little salt added to it, has cleared. Apparently a great affinity existed between the organic and the inorganic substances introduced into the water. The inorganic body abstracted the organic from the water, and in doing so, was deflocculated. Each particle as it was thrown off was enveloped in an aqueous jelly of the organic agent, or at least such was the working hypothesis I followed to arrive at my results, and I find it difficult to think of this breaking up stopping short of the final subdivision with the resultant separation into individual molecules, or the smallest particles into which a body can be subdivided without loss of identity.

As I have already stated, I deflocculated clay in the year 1901 and graphite in 1906 and immediately afterwards a number of other bodies. I early understood I was producing colloidal conditions of these bodies, but not until the summer of the present year, 1911, did I read any treatise on colloids, being familiar with this state of matter only in a very general way. During the summer I procured a copy of the book "Colloids and the Ultramicroscope" as written by by Dr. Richard Zsigmondy and translated into English by Jerome Alexander, of New York. I found the book extremely interesting, and at once wished to have a sample of my deflocculated graphite subjected to ultramicroscopic examination. Mr. Alexander kindly undertook the examination. He found the graphite in the deflocculated condition to be in a true colloidal state, the particles being in rapid motion, and he estimated their average size in linear dimensions to be 75 millimicrons. Seventy-five millimicrons are seventy-five millionths of a millimeter, and it would require slightly more than 13,000 of the particles to extend one millimeter. Now, the particles of disintegrated graphite, used as the crude material from which to produce deflocculated graphite, pass, as I have stated, through a sieve having 40,000 meshes to the square inch and their maximum linear dimensions are such that it would require 13 of them to extend one millimeter. Hence, the particle of disintegrated graphite is one thousand times greater in linear dimension than the deflocculated one. These

are figures that certainly test our powers of appreciation.

I have been asked, "Why don't you speak of the graphite as colloidal?" Knowing now that it is in a colloidal state, I speak of it as being colloidal, but when I am speaking of my process I am talking of a method of producing deflocculation. When does that process of deflocculation stop? Is it short of the final subdivision and the throwing off of the molecule? I think not. I believe we are here dealing with molecules. Their size may not agree with what they should be as computed in accordance with accepted theories, but, nevertheless, I cannot conceive the subdivision once started, in the presence of sufficient deflocculating agent, will stop short of the final, with the freeing of the molecule and the creation of the colloidal state.

How did all this I have been telling you come to happen? The following quotation aptly tells how:

"It's generally the fellow who doesn't know any better who does the thing that can't be done. You see the blamed fool doesn't know it can't be done, so he goes ahead and does it."

THE CHEMIST AND THE COTTON SEED OIL INDUSTRY IN AMERICA.[1]

By David Wesson.

Received November 14, 1911.

Few industries have made greater progress during the past forty years than the manufacture of cotton seed oil and by-products of the cotton seed.

Without indulging too much in statistics, we need only compare the amount of seed crushed in 1872—52,000 tons—with the average annual crush of the present time—4,000,000 tons.

To put it another way, in 1872 4 per cent. of 1,317,000 tons were crushed, while the average crush of to-day is 66⅔ per cent. of 4,000,000 tons. This put into dollars would mean that in 1872 the farmers received not over $8.00 per ton from the mills or $416,000 total, while at $20.00 per ton for seed, a conservative price for to-day, the mills are paying annually $80,000,000.

The growth of the industry is shown in the following table:

Year.	Seed worked.	Per cent. of crop.	50 gal. bbls. of oil.
1872	52,705	4	35,000
1880	235,404	9	175,000
1890	873,702	25	690,000
1900	2,479,386	53	1,920,000
1910	4,000,000	66	3,200,000

The rapid growth shown above is due to several causes, such as increase of population in the country and the increasing demand for edible fats in all parts of the world, but the chief cause has been the work of the chemist which has made the oil edible and has cheapened the cost of production, while the cost of the raw material, the cotton seed, has been constantly increasing.

[1] Presidential Address delivered before the Society of Cotton Products Analysts, Chemists' Club, New York, June, 1911.

When the speaker first saw crude cotton seed oil in the spring of 1884, the chemists employed by the oil mills and refineries could be counted on the fingers of one hand. If near chemists were included the fingers of both hands would have been sufficient.

Apparently the first chemists were employed in connection with the refineries, mill work being considered a mechanical problem pure and simple.

The refining methods at that time were very crude and purely empirical. Caustic soda solution was added in varying amounts according to the ideas of each individual refiner; in one case, for instance, the strength of the lye was judged by feeling a drop between the fingers.

The refining losses were tremendous. Oil was refined with 12–14 per cent. loss which now is easily handled inside of 8 per cent. The finished oil was as a rule tainted more or less by soap stock, and no two lots were alike. The refiner was entirely dependent upon the character of the seed for the color and flavor of his product. One season all oil might be prime, while next season most of the oil might be off.

White oils were produced in the early days by treating the yellow oil from alkali refining with sulphuric acid, followed by an alkaline wash. Some people used permanganate of potash or bichromate of potash and sulphuric acid. The resultant oil was white but not very edible.

In 1881–1882, fuller's earth was first used, making a white oil superior to that produced by what was called the acid treatments. It had a very poor flavor, but never the less large quantities were used in lard mixing.

The introduction of an improved method of refining the oil in 1900 has probably done more than any other factor to put the industry on its present basis.

By means of this refining method, which for trade reasons is kept secret, it is possible to turn out a perfectly neutral odorless product from the regular commercial oil, year in and year out, putting refined cotton seed oil so far as uniformity is concerned in the same class as granulated sugar.

The high standard of quality set by this process has made all large refineries improve their methods, and this has taken the oil from the soap kettle and put in on the table with consequent increase in value.

Now let us turn to the oil mill end of the business. The first systematic examination of mill products was begun in 1887, a year after the formation of the American Cotton Oil Trust. Samples from the different mills were examined regularly in the writer's laboratory, and the oil, ammonia and moisture determined in meal and cake. The hulls were also examined for meats and imperfect hulling. In those days the cake was sold on looks, soft yellow cake running 14 per cent. or so of oil being considered the best, while bright yellow meal, running about 10–12 per cent. of oil, was quite regular, though many mills did much better. Ten per cent. in cake was considered a fair basis for computing yields. I have before me analytical results from seven representative mills in Dec., 1888.

The lowest percentage of oil in meal was 8.75, while the highest was 13.37.

I also have here a table showing the yields of about fifty mills during the season of 1887–1888. The best oil production shown is 44.05 gallons with 783 lbs. of cake per ton, while the poorest is 33.69 gallons and 737 lbs. of meal or cake.

The highest cake production shown is 852.63, while the lowest is 636.38. These results compared with present methods calling for 900 lbs. of meal and not over 7 per cent. of oil left in the same show what an improvement has taken place in the work of the oil mills.

The change in mill results is mostly due to the chemist who by constantly testing the products has shown the losses, and made necessary constant improvements in machinery, and care in operating the same.

What the chemist has done for the oil mills as a whole can be figured in dollars and cents as follows: Old method of working made 800 lbs. of meal and left in it 10 per cent. of oil or 80 lbs. oil per ton of seed. Present methods make 900 lbs. of meal and leave 7 per cent. of oil or 63 lbs., a difference of 17 lbs. of oil saved per ton of seed worked. At 5 cents per lb. this means a saving of 85 cents per ton of seed, or $3,400,000 on the crop, without taking increased cake into consideration.

If we compare the old refining methods with the present ones, we find instead of 12 per cent. loss, an average of 8 per cent., 4 per cent. of 3,200,000 bbls. worth 5 cents per lb., $20.00 per bbl., or $2,560,000.

The conversion of soap stock into fatty acids and glycerine has raised the value of the fat therein at least 3 cents per lb., or $12.00 per bbl.

In refining 3,200,000 bbls. of oil, 7 per cent. would appear as fatty acids in soap stock—224,000 bbls., which, at $12.00 per bbl., would be worth $2,688,000.

By making the oil edible, $2.50 per bbl. is a conservative figure to put on the increased value of the oil on 3,200,000 bbls. This amounts to $8,000,000 a year.

If we sum up we find results as follows:

Improved mill work	$3,400,000
Improved refining	2,560,000
Improved soap stock value	2,688,000
Improved flavor of oil	8,000,000
Total annual increased value of oil mill products due to applied chemistry	$16,648,000

We might go further into the various products made from the oil and soap stock, but this is sufficient to show, though somewhat imperfectly, the value of our work to the oil mills. On the other hand, the increased quality of the oil has increased the demand for it, and the supply of raw material, the seed, being limited, has gone in value from $8.00 to $20.00 per ton or an increase of $12.00 per ton. 4,000,000 tons of seed at $12.00 a ton is $48,000,000 a year which goes to the farmer. In other words, chemistry applied to the oil mill business has done three times as much for the farmer as it has for the mills and refineries.

When we look back at our achievements, we feel something has been accomplished but we well know there is still a hard struggle before we get the business on a secure basis.

No sane miner would buy ore at $20.00 per ton without having every car very carefully sampled and assayed. He would pay for no more than its value as shown by analysis. With cotton seed, we all know how little attention is paid to its intrinsic value, and how little care is taken to sample it. One per cent. oil in the seed means $1.00 per ton difference in value, but who ever heard of seed being docked because it was poor in oil?

Meal is being more and more sold on analysis as it should be, but there is still much to be desired.

We have good methods for soap stock analysis, but we lack a strictly scientific and at the same time practical method for crude oil analysis. It is hoped we can some day in the near future obtain a method, the accuracy of which will be commensurate with the value of the product.

Let us continue our work, and, encouraged by the achievements of the past, endeavor to do better in the future, so we may all be proud of our membership in the Society of Cotton Products Analysts.

NOTES AND CORRESPONDENCE.

CORRECTION.

The Preparation and Properties of Metallic Cerium.

Editor of the Journal of Industrial and Engineering Chemistry:

In your Vol. 3, No. 12, December, 1911, pp. 880–897, appears an article by the writer on the "Preparation and Properties of Metallic Cerium." In justice to previous investigators, the writer would like to make the following corrections.

Bottom of page 881.—"The following year Hillebrand and Norton published.....chlorides of cerium and potassium." They used sodium-potassium chlorides and cerium chloride.

Bottom of page 881.—"They succeeded in producing about 6 grams of cerium." Should read, "They succeeded in producing about 6 grams of cerium at a single operation and produced in all about 30 grams of the metal."

Page 886. "Earlier work on the Electrolysis of the Anhydrous Chlorides." The method there described is that given by Moissan in his *Chimie Minerale* and is somewhat different from the process used by Hillebrand and Norton.

Page 891.—Under the heading "Physical Properties of Metallic Cerium" should be inserted the following: "Some of the physical and chemical properties of cerium have been determined by Hillebrand (*Pogg. Ann.*, **156**, 466 and **158**, 71) and by Muthmann (see references 23 and 24)."

Page 893. At the end of the last paragraph on the "Determination of the Melting Point" should be added: "The melting point determined by the writer corresponds fairly closely with the value given by Muthmann (623° C)."

Page 893. At the end of the paragraph on "Specific Heat" should be added. "Dr W F Hillebrand determined the specific heat of cerium by means of Bunsen's ice calorimeter (*Pogg. Ann.*, **158**, 71) He gives the corrected value of 0.04479

for pure cerium, using about 2 grams of metal in a determination. The writer used more than 70 grams of metal in a determination using Joly's differential steam calorimeter, and obtained a corrected value of the specific heat for pure cerium equal to 0.05112. The atomic heat using Hillebrand's value is 6.28; using Hirsch's value, 7.17."

Page 893.—At the end of the paragraph on "Heat of Oxidation" should be added. "Muthmann (Liebig's *Ann.*, **331**, 41) gives the heat of oxidation of cerium equal to 1603 cal. per gram."

Top of page 895.—At the end of the second paragraph under the heading "Alloys" should be inserted: "Muthmann and Beck (*24b*) have described some of the alloys of cerium with zinc, aluminum, magnesium and mercury."

Page 895.—Under "Aluminum Alloys" should be added: "Muthmann (Liebig's *Ann.*, **331**, 47) describes the compound $CeAl_3$."

Page 896.—Under "Mercury Alloys" should be added at the end of the paragraph: "Cerium will dissolve in mercury to the extent of about 15 per cent." ALCAN HIRSCH.

BROOKLYN, December 6, 1911.

THE MÉKER BURNER.

Editor of the Journal of Industrial and Engineering Chemistry:

The every-day tools of the chemist determine to a large extent the character of his work no less than those of the artisan do his. The success or failure of a great research problem in chemistry may depend as much upon the apparatus at hand as upon the imagination and skill of the worker. Possibly the leading fact in the history of science is this: that great trains of discoveries have depended more upon the invention of new apparatus than upon the development of the human brain. After all it is the attention to the details of equipment as well as the personal organization in a laboratory, which brings about perfect results. And so we sing the praises of the Méker burner. With this burner one can do almost the work of the blast-lamp, without the annoyance connected with the use of the latter. The flame is large and intensely hot and the highest temperature, strange to say, is reached at the base of the flame. For analytical work in crucibles it has no equal, nor is there any other device approaching it in excellence. It has no inner cone and platinum ware can be made to receive the full effect of the flame without danger of injury. "There is nothing new in the apparatus—no original idea involved," many a critic would say, "just a Bunsen burner with an abundant air supply and a piece of Davy safety-lamp gauze at the top." But not every burner so constructed will give a flame free from the destructive inner cone, and intensely hot at the base. Every point in the design must be carefully balanced to produce the perfect result. We do not know the inventor or the history of his invention, but a simple inspection of the burner in action indicates that this is no chance discovery, no day-dream or night-dream suddenly made concrete and perfect. Carefully thought out and wrought out by trial and experiment and repeated experiment is the perfectly simple Méker burner.

W. D. RICHARDSON.

IMPORTS AND EXPORTS OF FARMERS' MATERIALS.

The agricultural interests of foreign countries buy nearly $100,000,000 worth of American manufactures and other products for use in cultivating the soil, while about $50,000,000 worth of foreign products are annually imported into the United States for use upon American farms. The foregoing summarizes certain information recently compiled by the Bureau of Statistics, Department of Commerce and Labor.

The exports from the United States of articles required in farming, the larger portion are composed of manufactures, such as agricultural implements, binding twine, barbed wire, and oil cake, while phosphate rock to be ground up and used as fertilizer, and clover, timothy and other grass seeds are among the articles exported in the natural state. In addition to the exports above enumerated as specifically for farm use, there are certain articles for which the agriculturalists of all other countries draw upon the United States but which cannot be classed as distinctively for farm purposes, such as wagons, carriages, traction engines, fiber bags, pumps, etc. In such cases the Bureau of Statistics has no means of determining the proportion of the exports intended for farm use and they are not, therefore, included in the $100,000,000 worth of merchandise exported for agricultural purposes.

Taking up the principal exports of the class under discussion, agricultural implements head the list, with a probable total of $40,000,000 in the year about to end, comprised of nearly $20,000,000 worth of mowers and reapers, $8,000,000 worth of plows and cultivators, $2,500,000 worth of threshers, and the remainder miscellaneous farming tools and implements. These agricultural implements are exported to practically all parts of the world where man has adopted modern methods of cultivating the soil: the great wheat fields of Russia, in the vineyards of France, on the coffee plantations of Brazil, in the rice fields of China and Japan, and in all the rapidly developing countries of the New World, including Canada, Argentina, Cuba, and Mexico. The year's exports will range nearly $8,000,000 to European Russia, $6,000,000 to Argentina, and about $5,000,000 to Canada, to about $1,500,000 to Africa, while to British Australasia and Oceania will be sent a total of nearly $2,000,000 to other Oceania and Asia about $1,000,000, and Brazil about $500,000 worth. Even the great manufacturing countries of Europe, the United Kingdom, Germany, and France, are represented in the year's exports of agricultural implements, the United Kingdom with a total of over $1,000,000, Germany, $2,000,000, and France, $3,000,000.

Fertilizers, of which the exports will be about $12,000,000 during the year, are chiefly sent to European countries, where long-continued use of the soil has largely depleted their natural fertility and rendered artificial fertilizers a necessity. For American phosphate rock and other fertilizers of that class Germany is the largest market, followed next by Netherlands and the United Kingdom. Another class of materials, used as cattle food, whose exports are considerable includes oil cake and oil cake meal made from cottonseed and linseed. Of these the exports amount to about $15,000,000 per annum, being exported mostly to various countries of Europe.

Binding twine is another article of importance in wheat-growing countries. Of that article the year's exports will be about $8,000,000, practically all destined for Russia and other European countries, Canada, and Argentina. American barbed wire exported, about $5,000,000 per annum, goes chiefly to Canada, Australia, Argentina, British Africa, Mexico, Brazil, and Cuba. In addition to these articles, there are others largely if not exclusively required by farmers, such as windmills, with exports nearing $2,000,000 per annum; and clover and other grass seeds, over $1,000,000.

On the other hand, American farmers draw upon other countries for certain of their requirements, most of the imports, however, being articles in their natural state. The largest item shown in the imports of last year were fertilizers, including nitrate of soda, $17,000,000; guano, manure salts, etc., $10,000,000; potash salts, $8,000,000; sulphate of ammonia, used in part as a substitute for manure and in part in the manufacture of alum, $5,000,000; animals for breeding purposes, chiefly horses, nearly $3,000,000; clover seed, $3,000,000; and sugar beet seed, $750,000.

WHAT OUR RIVERS CARRY.

Colorado River discharges during an average year into the Gulf of California 338,000,000 tons of mud and silt as suspended matter. In addition to this the dissolved substances in the water include 4,550,000 tons of sodium chloride, or common salt; 3,740,000 tons of Glauber's salts; 4,000,000 tons of lime; 2,400,000 tons of gypsum; and 4,800,000 tons of Epsom salts. In spite of all this dissolved material the Colorado at its mouth is not considered to be a stream of unusually high mineralization for that region of the country. The reason is that the river also carries so enormous an amount of water that the dissolved salts constitute a comparatively small proportion of the total discharge. Other streams in the country contain dissolved salts in greater concentration—for example, the Elm Fork of Red River, in Oklahoma, discharges nearly 1,300,000 tons of common salt annually. Although this amount is not so great as that discharged by the Colorado it is much greater in proportion to the size of the area drained. The discharge of salt from the Colorado is equal to 20 tons annually to each square mile drained by the river, but the salt in Elm Fork of Red River is equal to 1,680 tons per square mile of area drained. The same river discharges annually 177,000 tons of magnesium chloride, 168,000 tons of Epsom salts, 690,000 tons of gypsum, and 54,000 tons of lime. These quantities, too, are considerably greater than those carried in the Colorado in proportion to the size of the drainage area.

Belle Fourche River, at Belle Fourche, S. Dakota, discharges 191,000 tons of gypsum, 79,000 tons of Glauber's salts, and 236,000 tons of Epsom salts. The mud and silt carried in suspension by this river amount to 1,100,000 tons. Milk River at Havre, Montana, discharges annually 41,000 tons of soda; Payette River, in Idaho, discharges 46,000 tons; Salt River at Roosevelt, Arizona, discharges 288,000 tons of salt and 170,000 tons of Epsom salts; and the Rio Grande discharges 245,000 tons of lime and 368,000 tons of Glauber's salts.

The foregoing are a few of the figures of incidental interest presented by Water-Supply Paper 274 of the United States Geological Survey, entitled "Some Stream Waters of the Western United States." The work reported by this volume is, however, of higher practical importance than the above statement would indicate. It is the result of an investigation of the quality of western stream waters made for the purpose of determining their availability for use for irrigation and other purposes. For a water-supply system the quality of the water available determines its usefulness quite as much as the quantity. Some waters contain ingredients that make it impossible to use them for irrigation unless certain precautions are taken in applying them to the land and in draining them off. Certain ingredients in water make it unavailable or destructive if used in boilers and the quality of water used in a manufacturing plant may very largely determine the quality of the product of manufacture. The report just published therefore can not fail to be of material value to the manufacturing and agricultural interests of the West; and the proper consideration of the information that it contains will prevent many costly mistakes in connection with the industrial development of that part of the country.

CEMENT PRODUCTION TO 1910.

Ten years ago the production of Portland cement for the first time passed the 10,000,000-barrel mark, showing an increase of 2,600 per cent. over the production of 10 years previous, and the giant strides that had been made in the industry were widely remarked. Even this production was small compared with that of the present day. In 1910, according to the report on cement by Ernest F. Burchard, of the Geological Survey, the production of Portland cement reached the enormous total of 76,549,951 barrels, with a value of $68,205,800. This is equivalent to 12,986,152 long tons, valued at $5.25 a ton. It is an increase over the output for 1909 of 11,558,520 barrels, or nearly 18 per cent., and an increase in value of $15,347,446, or more than 29 per cent. This increase alone is greater than the total output of Portland cement in 1900. In addition to Portland cement there was also produced last year 1,139,239 barrels of natural cement and 95,951 barrels of puzzolan cement, a total of 77,785,141 barrels.

The price of Portland cement in 1910 was as low as 73 cents a barrel in some places, the average for the United States being 89.1 cents a barrel. In 1890 the average price was over $2 a barrel and as late as 1903 it was $1.24 a barrel.

Mr. Burchard remarks that measured by the capital invested the cement industry is one of the world's three great extractive industries. In capital employed it apparently far outranks the gold-mining industry of the United States, including Alaska, as well as the copper industry. Only coal and iron stand ahead of it.

The principal constituent of Portland cement is limestone, and Mr. Burchard's report summarizes the most important limestone formations in all the States. The greatest of these are found in the eastern half of the United States, where there are enormous limestone deposits. The report is accompanied by a map showing the distribution of these limestones. The areas they cover comprise many thousands of square miles. The map also shows the location of the operating cement plants in the United States.

That the manufacture of cement is an American industry is shown by the fact that while our production last year was over 75,000,000 barrels our imports were only 306,863 barrels. Our exports were 2,475,957 barrels.

The following table shows the healthy growth of the American Portland cement industry and also the decrease in prices:

PRODUCTION OF PORTLAND CEMENT IN THE UNITED STATES 1880 1910.

	Barrels.	Average price per barrel.
1880	42,000	$3.00
1890	335,500	2.09
1895	990,324	1.60
1900	8,482,020	1.09
1905	35,246,812	0.94
1909	64,991,431	0.81
1910	76,549,951	0.89

WORLD'S PRODUCTION OF COAL.

The total coal production of the world in 1910 was approximately 1,300,000,000 short tons, of which the United States contributed about 39 per cent. According to the United States Geological Survey, it exceeded Great Britain, which ranks second, by over 200,000,000 tons. Great Britain's production in 1910 was less than 60 per cent. of that of the United States, and Germany's was less than half. The increase in both of these countries in 1910 over 1909 was comparatively small, whereas the increase in the United States was nearly equal to the entire production of France and was more than the total production of any foreign country except Great Britain, Germany, Austria-Hungary, and France.

The United States has held first place among the coal producing countries of the world since 1899, when it surpassed Great Britain. In the 11 years since 1899 the annual output of the United States has nearly doubled, from 253,741,192 short tons to 501,596,378 tons, whereas that of Great Britain has increased only 20 per cent., from 246,506,155 short tons to 296,007,699 tons.

The following table shows the coal production of the principal

countries of the world in 1910, except those for which only the 1909 figures are available

United States (1910)	501,596,378
Great Britain (1910)	296,007,699
Germany (1910)	245,043,120
Austria-Hungary (1909)	54,573,788
France (1910)	42,516,232
Belgium (1910)	26,374,986
Russia and Finland (1910)	24,967,095
Japan (1909)	16,505,418
Canada (1910)	12,796,512
China (1909)	13,227,600
India (1909)	13,294,528
New South Wales (1909)	7,862,264
Spain (1909)	4,546,713
Transvaal (1910)	4,446,477
Natal (1910)	2,572,012
New Zealand (1909)	2,140,597
Mexico (1909)	1,432,990
Holland (1909)	1,235,515
Queensland and Victoria	1,119,708
Italy (1909)	611,857
Sweden (1909)	272,056
Cape Colony (1909)	103,519
Tasmania (1909)	93,845
Other countries	5,236,903
Total	1,278,577,812

THE MINERAL PRODUCTION IN NORTH CAROLINA DURING 1908–10.

The North Carolina Geological and Economic Survey has just sent to the Public Printer a report on the mining industry in North Carolina for the past three years.

Of the metallic minerals, iron holds first place in the table of production and gold and silver next.

Of the non-metallic minerals, clay products, building stones, mica, and talc are prominent in their production in the order named. There has been a considerable decrease in the production of monazite, owing to the fact that thorium salts are imported cheaper than they can be produced in this country.

The table below gives the production of each mineral during 1908, 1909, and 1910:

Mineral.	1908.	1909.	1910.
Gold	$ 97,495	$ 43,075	$ 68,586
Silver	668	324	4,888
Copper	2,560	29,186	17,845
Iron	76,877	107,013	114,237
Garnet	4,052	9,188	7,981
Millstone			
Mica { Sheet	114,540	122,246	193,223
Mica { Scrap	13,330	26,178	37,237
Precious stones	570	479	700
Monazite	37,224	46,928	10,104
Zircon	.....	250	.....
Talc and Pyrophyllite	31,443	77,983	69,805
Mineral waters	27,163	20,558	21,389
Stone	824,927	850,807	920,027
Sand and gravel	2,070	13,358	13,406
Clay products	944,317	1,302,611	1,223,704
Miscellaneous[1]	109,880	133,642	145,314
Totals	$2,307,116	$2,783,826	$2,848,446

CHIEF GEOLOGIST, GEOLOGICAL SURVEY.

The Geological Survey announces the appointment of Waldemar Lindgren as chief geologist, to succeed C. Willard Hayes, who recently resigned from the Survey. Mr. Lindgren has been a member of the Federal Survey since 1884 and has been in charge of its investigations in metalliferous deposits since 1907. He is the author of some fifty reports published by the Survey and in addition has contributed between fifty and sixty articles to technical and scientific journals. Mr. Lindgren is a trained mining engineer and has a world-wide reputation as an authority on the geology of ore deposits

[1] Includes barytes, sand-lime brick, and kaolin productions.

NATION'S COAL PRODUCTION.

The Geological Survey has issued its annual coal chart, showing the production of coal by States from the year 1814–1910. The figures relate a wonderful history of growth. In 1814 a total of 22 tons of coal was produced in Pennsylvania. In 1815 the percentage of increase was good but still only 50 tons were taken out. By 1825 100,000 tons were mined in the two States producing. In 1850 the figure had reached 7,018,181 tons. In 1876 it was 53,280,000 tons. At the end of the century it was 269,684,027 tons. In 1905 it was 392,722,635 tons. In 1907, which it was supposed would remain the record year for some time, the production was 480,363,424 tons, but in 1910 the enormous total was reached of 501,596,378 short tons, a production larger by far than that of any other country in the world. The total production since 1814 has been approximately eight and a quarter billion tons

CUBA IRON-ORE PRODUCTION.

The shipments of Cuban iron ores, according to statistics collected by the Geological Survey, show the output for 1910 of 1,417,914 long tons, as against 930,446 tons for 1909, the greatest previous production. In 1900 the production was 446,872 tons. The ores are obtained from deposits near Santiago. Cuba is now the fifth largest producer of iron ore in the world, being exceeded only by the United States, Germany, the United Kingdom, and France.

GREATEST IRON PRODUCING REGION IN THE WORLD.

The Mesabi Iron Range in Minnesota produced in 1910, according to the Geological Survey, 53 3/4 per cent. of the entire iron-ore production of the United States. The Lake Superior district, including Minnesota, Michigan, and Wisconsin, produced 81 1/2 per cent. of our total iron-ore production. Figures from other countries are not yet available for 1910, but this is probably a greater production than the entire year's output for any foreign country.

ILLINOIS COAL PRODUCTION.

Illinois has produced more coal than any other State except Pennsylvania, the total tonnage since 1833, when coal mining first began in the State, being 790,333,235 short tons, according to the Geological Survey. Last year the production was 45,900,246 tons and the State stood third, Pennsylvania producing 235,006,762 and West Virginia 61,671,019 tons.

COAL EXPORTS IN 1910.

The exports of coal from the United States during 1910, according to the United States Geological Survey, were 13,805,866 long tons, valued at $41,470,792. Of this quantity 3,021,627 long tons, valued at $14,785,387, was anthracite, and 10,784,239 long tons, valued at $26,685,405, was bituminous coal.

The imports of anthracite amounted in 1910 to only 8,195 long tons, valued at $42,244, and those of bituminous coal to 1,497,709 long tons, valued at $3,975,561.

OIL IN ALASKA.

Petroleum has been found in Alaska, and while there has been practically no production, it is not impossible, according to the United States Geological Survey, that commercial pools may be found. Oil seepages occur on the west shore of Cook Inlet, on the east side of the Alaska Peninsula, and on Controller Bay, all close to tidewater, and hence capable of cheap development.

PURE FOOD AND DRUG LAW IN MONTANA.

The Pure Food and Drug Law enacted by the Twelfth Legislature of Montana was put into force on January 1, 1912. The administration of the law is made a duty of the State Board of Health. A food and drug laboratory has been provided for in connection with the Department of Chemistry of the Montana State College at Bozeman. The organization of the laboratory staff is as follows:

W. M. Cobleigh, State Chemist; C. E. Mollet, Director of Drug Analyses; Drury L. Weatherhead, Food Analyst; D. B. Swingle, Bacteriologist.

BUREAU OF MINES APPROPRIATIONS.

In the general estimates for appropriations for the fiscal year 1912, which begins July 1, 1912, Secretary of the Interior, Walter L. Fisher, has recommended the following items for the Bureau of Mines:

For the investigation as to the causes of mine explosions, methods of mining, especially in relation to the safety of miners, the appliances best adapted to prevent accidents, the possible improvement of conditions under which mining operations are carried on, the use of explosives and electricity, the prevention of accidents, and other inquiries and technologic investigations pertinent to the mining industry, $360,000.

For the investigation, analyzing and testing of the coals, lignites, and other mineral fuel substances belonging to or for the use of the United States, $135,000.

For the investigations into the treatment of ores and other mineral substances, with special reference to the prevention of waste in the mining and utilization of important mineral resources, $100,000.

For the investigations of the coals of Alaska, with reference to their mining, transportation, and utilization, $50,000.

CIVIL SERVICE EXAMINATION.

The United States Civil Service Commission announces an examination on January 17–18, 1912, to secure eligibles for assistant chemist in the Bureau of Chemistry, Department of Agriculture, at salaries ranging from $1,200 to $1,600 per annum.

The usual entrance salary is $1,200, and only in exceptional cases of unusual qualifications, including considerable valuable experience, will a higher entrance salary than $1,200 be paid. No assurance regarding promotion is given, but during recent years industrious men of average ability have received during the first five or six years of service promotions aggregating at the rate of about $100 a year.

Qualified persons are urged to enter this examination as the opportunities for appointment are excellent. Of the thirty-eight persons who passed the assistant chemist examination held in April, 1911, the three highest on the list were appointed at $1,440 per annum, and twenty-seven others were tendered appointment at $1,200 per annum.

For detailed information interested inquiries are referred to the U. S. Civil Service Commission, Washington, D. C.

The International Petroleum Commission will hold its meeting January 16–22, 1912, in Vienna, with headquarters at the Engineers and Architects Club.

This commission will be divided into three parts, which will discuss the general and special phases of the petroleum industry. The first division will take up the general methods of analysis of crude oil, benzine, petroleum lubricating oils, paraffins and other products. The second division will discuss the scientific nomenclature, and the third will give its attention to the subject of storage, safety and transportation.

The entertainment committee has made arrangements for receptions, excursions to refineries and oil wells, etc.

Dr. F. W. Frerichs, President of the American Institute of Chemical Engineers, has been elected an honorary member of the Chemical Metallurgical and Mining Society of South Africa

BOOK REVIEWS.

Handboek ten Dienste van de Suikerriet-Cultur en de Reitsuikerfabricage op Java. Derde Deel. De Fabricatie van Suiker uit Suikerriet op Java. Tweede druk. door H. C. Prinsen Geerligs. Director der Filiale Nederland von het Proefstation voor de Java Suiker Industrie, 1911, 512 pages. Price, bound f. 7.50. Edited by the United Sugar Experiment Station of Java. Amsterdam. J. H. de Bussy.

The first edition of this work by Mr. Geerligs was reviewed in This Journal, 1, 380. The importance of the volume to the cane sugar industry was recognized in all parts of the world; an English translation, published by the International Sugar Journal, appeared in 1909 and a Spanish translation in 1910. Those who have become familiar with this volume of the handboek series will welcome the appearance of a new edition of the Dutch original.

The scope of the present volume is best stated by Mr. Geerligs in his preface: "While the purpose of this second edition is the same as that of the previous one, certain sections of the book, such as clarification of juice, boiling, and working up of massecuite, have been entirely revised in order to bring the subject matter fully up to date with the growing practice of making only first sugar and of avoiding after-products. The section of the book relating to calculation and interpretation of factory results has also been rewritten in order to include the latest observations of sugar house experience."

Comparing the second with the first edition of Vol. 3 of the

handbook the addition of some 10 new pages is noted in the part relating to the chemical composition and distribution of the constituents of the sugar cane. The second division of the book relating to processes of extraction, utilization of bagasse, defecation, filtration, evaporation, boiling, etc., has been entirely rewritten. The recent development in processes of sugar manufacture is shown by the fact that this part of the volume has been increased from 304–365 pages. This section of the book has also been improved by the introduction of over 40 cuts and photographs illustrating the latest improvements in sugar house equipment. A particularly valuable feature of the new edition is the comprehensive tables and charts which give the results of 130 Java sugar factories for the 1910 campaign.

The typography of the book conforms to that of the other volumes of the handbook and is excellent in every respect.

It is hoped that the English translation of Mr. Geerligs' book may also soon appear in a new edition and include the numerous improvements which have been noted in the original.

C. A. BROWNE.

The Manufacture of Sulphuric Acid and Alkali. By GEORGE LUNGE, Volume III, Third Edition, 764 pages. D. Van Nostrand Company, New York. Price, $10.00.

Professor Lunge's books are too widely and favorably known to require detailed discussion. This third edition of Volume III is devoted to alkali making, and the chlorine industry in so far as they are strictly chemical processes. The electrochemical processes which have developed to such great proportions since the last edition (1896) are not included in this book, but are being treated in a separate volume, IV, by Professors Askenasy and Haber.

The third edition is more complete in its details and introduces much new matter. It is necessarily more bulky than the former editions and still includes many descriptions of processes of doubtful commercial value. It has been the consistent aim of the author, in this as in all volumes, to present as complete a record as possible of development of the industry. Students must know about the failures as well as the successes in an industrial development and will therefore find Professor Lunge's plan of selecting material very helpful.

The volume is divided into three general sections: (1st), Ammonia Soda Process; (2nd), Various Processes of the Alkali Manufacturing; (3rd), The Chlorine Industry. These subjects are treated under chapters including full references and illustrations of apparatus and plant arrangement.

A statistical appendix is a feature of the volume which is of value in establishing the relative importance of the branches of this industry. It is to be regretted, however, that the data here given is from six to fifteen years old. The exportation of chemicals from Great Britain (1738) in 1895 may fall far short of representing conditions to-day and the prices of soda crystals in 1889 have little value except to show that the ammonia soda was dropping.

A carefully compiled index will be greatly appreciated by us. The volume is well executed and conforms to the style and binding of the previous editions.

The technical chemists have always received the publication of this author with hearty approval, and we should be doubly appreciative for this most recent addition to the works on this great chemical industry.

M. C. WHITAKER.

Die Metallurgie des Wolframs mit besonderer Berucksichtigung der Elektrometallurgie. DR. HANS MENNICKE. 416 pages, 39 illustrations. Price, 17 Marks. Berlin: M. Krayn.

To many it will seem almost incredible that the metallurgy of tungsten requires so bulky a volume, yet the development of this metal has been so rapid within the last ten or fifteen years that it can no longer be classed as "rare." The book is intended primarily as a handbook and since it is the first of its kind it will be welcomed not only by the student but also by steel metallurgists and incandescent lamp manufacturers. Among the chapter headings are: Tungsten Ores; Reduction Methods; By-Products, including Molybdenum, Copper, Tin, Scandium, Titanium, Tantalum and Niobium; Manufacture of Sodium Tungstate, Tungstic Acid, Alloys of Tungsten, Tungsten Bronzes, Tungsten Filaments; Methods for Fireproofing Cotton and other fabrics; Analytical Methods. Although the chapters on tungsten steel and on tungsten filament manufacture are comparatively brief and the information based largely on patent literature, the chapters on the production of tungsten powder are particularly well treated, the author having had considerable experience in this line. A long list of references to patent and journal literature is appended.

C. G. FINK.

Annual Tables of Constants and Numerical Data (Chemical, Physical and Technological). Vol. I. Compiled and published by an International Commission, appointed by the Seventh International Congress of Applied Chemistry (see *Jour. Am. Chem. Soc.*, August, p. 105, of the Proceedings).

The first volume of the annual tables will contain all the constants and numerical data, collected by the Abstractors of the International Commission from more than 300 periodicals belonging to Chemistry, Physics and Allied Sciences, Pure and Applied, which were published during the year 1910. The tables will form a volume of about 400 pages, arranged in sections. The wide range of scientific and technical literature which is covered by the annual tables cannot fail to be of value to the scientific men, and will be a valuable addition to every library.

Subscriptions should be filed before January 15, 1911. Subscription blanks, terms of subscription and descriptive leaflets may be obtained from any one of the three American Commissioners: Dr. G. N. Lewis, Mass. Institute of Technology, Boston, Mass.; Professor G. F. Hull, Dartmouth College, Hanover, N. H.; and Professor J. Stieglitz, University of Chicago, Chicago, Ill.

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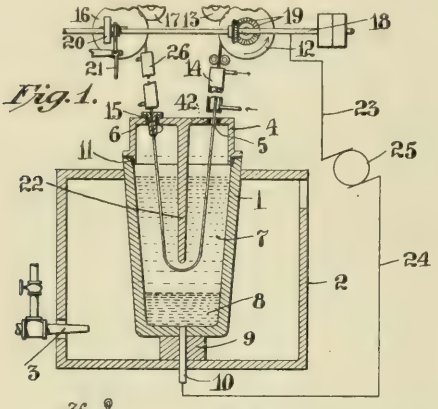
RECENT INVENTIONS.

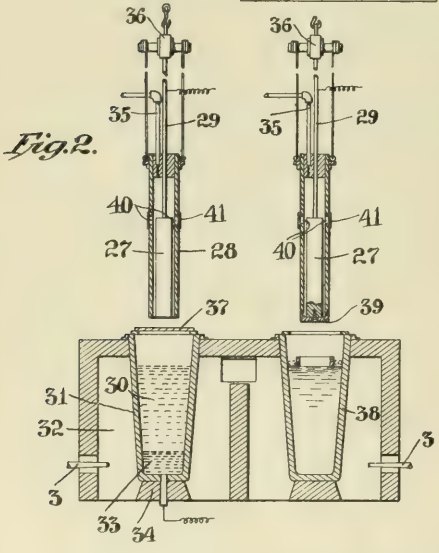
Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

PROCESS OF AND APPARATUS FOR MAKING CLAD METALS.

U. S. Patent No. 1,004,673, to John E. Monnot, New York City. Assignor to Duplex Metals Company, of New York City.

This invention relates to processes of and apparatus for producing clad metals, and it comprises a process of producing clad metals wherein a core or base of ferrous or like metal is given a dense, cohering, impervious coating of an unlike, high-melting, ductile metal by electro-depositing said unlike metal thereon in a molten state; all as more fully hereinafter set forth and claimed.





The process consists in immersing a high-melting metal body in a solution of a salt of an unlike metal and thereby producing a striking coating of the unlike metal, and then making such metal body a cathode in a bath of fused electrolyte containing a dissolved ductile high-melting different metal, such bath being maintained at a temperature above the melting point of such high-melting metal.

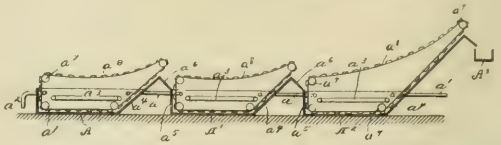
The accompanying illustration shows apparatus in which the process is carried out.

METHOD OF PRODUCING CRYSTALS.

U. S. Patent No. 1,004,858, to Herbert H. Dow, Midland, Mich. Assignor to the Dow Chemical Company, of Midland, Mich.

This invention relates to the manufacture of chemical products of a crystalline nature.

The process consists in producing crystals by conducting the evaporation in two or more successive stages, and mechanically moving the precipitated crystals through the said stages in a



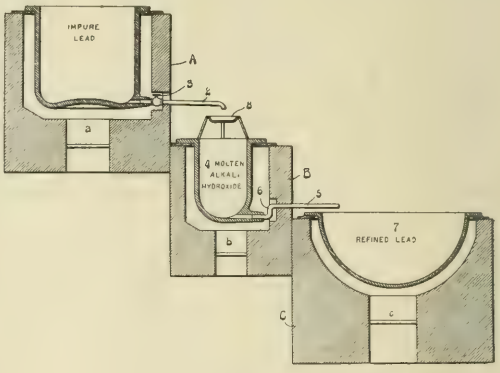
direction passing from a late stage of evaporation toward and through the earlier stages whereby the crystals formed in the later stages are washed in the purer liquor of earlier stages while evaporation is progressing therein.

The accompanying illustration shows apparatus in which the process is carried out.

PROCESS OF REFINING LEAD AND LEAD ALLOYS.

U. S. Patent No. 1,006,323, to Leland E. Wemple, St. Louis, Mo. Assignor one-half to Hoyt Metal Company, of St. Louis.

This invention is a process for the removal of contaminating metals or foreign elements from pig lead and from alloys of lead and antimony, of lead and tin, and of lead antimony and tin, and particularly to the removal of arsenic antimony, or tin, from lead, and to the removal of arsenic from antimonial lead or antimony-lead alloys, and from lead-tin-antimony alloys without the removal of either antimony or tin from the alloys.



The process consists in bringing the lead, or lead alloy containing impurities, or foreign elements, while in a molten state, in intimate contact with the hydroxid of an alkali, such as hydroxid of sodium, or hydroxid of potassium whereby the foreign elements are attacked by said hydroxid while the metallic lead itself is practically unattacked, and therefore remains in the metallic state, the contaminating metals undergoing a chemical change which is regarded as oxidation or at least partial oxidation, combining with or becoming held mechanically by the hydroxid.

The process may be carried out in the apparatus shown in the accompanying illustration.

METHOD OF PRODUCING NITROGEN COMPOUNDS FROM CARBIDS.

U. S. Patent No. 1,006,927, to Albert R. Frank, of Halensee, near Berlin. Assignor to Societa Generale Per La Cianamide, of Rome.

This invention is a method of producing nitrogen compounds from carbids, such, for instance, as cyanamids (carbodiimids), cyanids, nitrids, and other like compounds, as applied to the production of which the process would be illustrated by the formula

$$CaC_2 - 2NCaCN_2 - C,$$

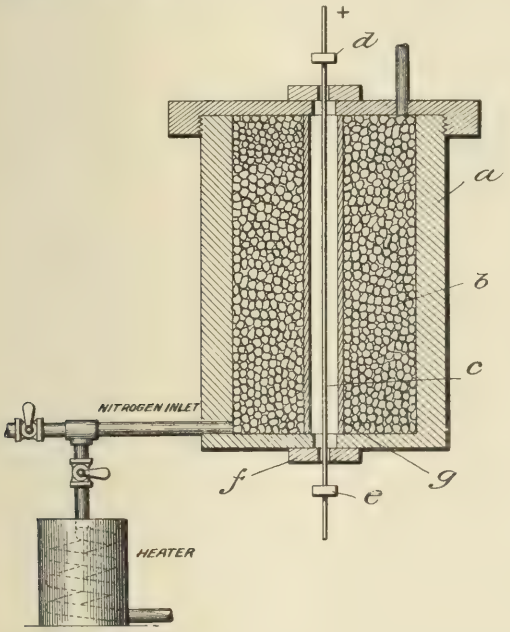
or

$$BaC_2 - 2NBaC_2N_2,$$

or

$$3MgC_2 - 2NMg_3N_2 - 6o.$$

The process consists in bringing a relatively small part of the carbid mass in a finely divided condition into contact with heated nitrogen to heat said carbid to the reaction temperature, supplying nitrogen as the reaction proceeds, thereby maintaining the temperature and continuing the reaction throughout the mass to be converted.



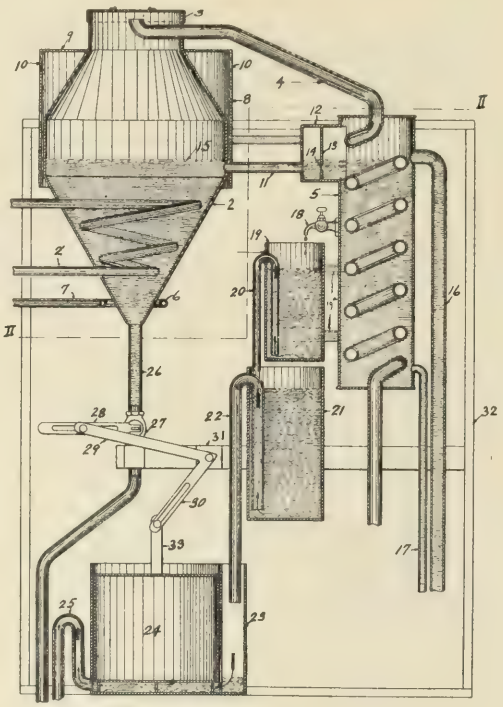
The accompanying illustration shows apparatus in which the process may be carried out.

A SELF-CLEANING STILL.

U. S. Patent No. 1,010,508, to W. H. McCune, Vandergrift, Pa.

This invention relates to an apparatus more particularly used for distilling water, with a mechanical arrangement for cleaning at intervals without substantial interruption of the process of distillation or the attention of an operator. It is planned to obviate the usual difficulties of interruption and loss of efficiency in distillation by so designing the apparatus as to clean automatically at regulated intervals.

The accompanying illustration is a sectional elevation, showing the distilling apparatus constructed and arranged in accordance with this invention. The new and automatic feature of this device is shown in parts 19, 20, 21, 22, 23 and 24, and the opening and closing of the flushing valve is accomplished by means of a float. The frequency with which the retort is drained is regulated by the volume of water discharged from the chamber into the tank 19 by drip cock 18.



MARKET REPORT.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF DECEMBER.)

Full List of Weekly Quotations, see "Oil, Paint & Drug Reporter."

ORGANIC CHEMICALS.

Acetanilid	Lb.	20½	@	23
Acetone (drums)	Lb.	13¾	@	15
Alcohol, grain (188 proof)	Gal.	2.56	@	2.58
Alcohol, wood (95 per cent.)	Gal.	50	@	52
Alcohol, denatured (180 proof)	Gal.	40	@	42
Amyl Acetate	Gal.	3.00	@	3.25
Acetic Acid	C.	1.75	@	1.90
Aniline Oil	Lb.	10¾	@	11½
Benzoic Acid	Oz.	11¼	@	12
Carbon Tetrachloride (drums)	Lb.	7¾	@	8¼
Carbon Bisulphide	Lb.	5	@	7
Chloroform	Lb.	23	@	28
Carbolic Acid (drums)	Lb.	19	@	20
Citric Acid (domestic)	Lb.	38½	@	39
Camphor (refined in bulk)	Lb.	—	@	44
Dextrine (imported potato)	Lb.	6	@	7
Dextrine (corn)	C.	3.08	@	3.25
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	16	@	16½
Iodoform	Lb.	2.95	@	3.00
Oxalic Acid	C.	7¼	@	7½
Pyrogallic Acid (bulk)	Lb.	1.25	@	1.48
Salicylic Acid	Lb.	32	@	34
Starch (corn)	C.	2.00	@	2.15
Starch (potato)	Lb.	5¼	@	5½
Starch (rice)	Lb.	7	@	8
Starch (wheat)	Lb.	4⅞	@	5¼
Tannic Acid (regular in bulk)	Lb.	68	@	70
Tartaric Acid, crystals	Lb.	30¼	@	30¾

INORGANIC CHEMICALS.

Acetate of Lime (gray)	C.	2.00	@	2.05
Acetate of Lead (brown, broken)	Lb.	7¾	@	8
Alum (lump)	C.	1.75	@	2.00
Ammonium Carbonate, domestic	Lb.	8	@	8¾
Ammonium Chloride, gray	Lb.	6⅛	@	6⅜
Aluminum Sulphate	Lb.	90	@	1.75
Ammonium Vanadiate	Oz.	41	@	50
Aqua Ammonia (drums) 16°	Lb.	2¼	@	2½
Arsenic, white	Lb.	2⅜	@	2⅝
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Barium Chlorate	Lb.	15	@	17
Barium Chloride	C.	1.90	@	2.25
Barium Nitrate	Lb.	5½	@	6¼
Borax, crystals (bags)	Lb.	3½	@	4
Boric Acid, crystals	Lb.	7	@	7½
Bromine, bulk	Lb.	25	@	30
Bleaching Powder (35 per cent.)	C.	1.25	@	1.30
Barytes (prime white, foreign)	Ton	18.50	@	22.50
Blue Vitriol	Lb.	4½	@	4¾
Calcium Chloride	C.	65	@	90
Calomel, American	Lb.	91	@	93
Chalk (light precipitated)	Lb.	4½	@	6
Cobalt Oxide	Lb.	80	@	1.00
China Clay (imported)	Ton	11.50	@	18.00
Feldspar	Ton	8.00	@	12.00
Fuller's Earth, powdered	C.	80	@	85
Green Vitriol (bags)	C.	60	@	85
Hydrochloric Acid (18°)	C.	1.15	@	1.55
Hydrochloric Acid (22°)	C.	1.45	@	1.75
Iodine (resublimed)	Lb.	2.60	@	2.65
Lead Nitrate	Lb.	8	@	8⅝
Lithium Carbonate	Lb.	60	@	63
Magnesite (raw)	Ton	10.00	@	11.00
Mercuric Chloride	Lb.	82	@	85
Nitric Acid, 36°	Lb.	3⅞	@	4¼
Nitric Acid, 42°	Lb.	4⅞	@	5¼
Phosphorus	Lb.	45	@	1.00
Phosphoric Acid, s. g. 1.75	Lb.	22	@	26
Plaster of Paris	C.	1.50	@	1.70
Potassium Bromide	Lb.	31	@	34
Potassium Permanganate (bulk)	Lb.	9⅜	@	10¾
Potassium Cyanide (bulk)	Lb.	20	@	24
Potassium Iodide (bulk)	Lb.	2.10	@	2.15
Potassium Chlorate, crystals	Lb.	8¼	@	9½
Potassium Nitrate (crude)	Lb	4½	@	5
Potassium Bichromate, 50°	Lb.	7⅜	@	7¾
Pumice Stone	Lb.	2	@	4
Quicksilver	Lb.	62	@	64
Salt Cake (glass-makers)	C.	55	@	65
Silver Nitrate	Oz.	36	@	38
Soapstone in bags	Ton	10.00	@	12.00
Sodium Acetate	Lb.	4¼	@	5
Sodium Chlorate	Lb.	8¼	@	9½
Sodium Bicarbonate (English)	Lb.	2¾	@	3
Sodium Bichromate	Lb.	5⅝	@	6
Sodium Bisulfite (not incl. pkg.)	C.	75	@	1.37½
Sodium Hydroxide, 60 per cent	C.	1.80	@	1.85
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent., spot	C.	2.20	@	2.22½
Sodium Silicate (liquid)	C.	65	@	1.50
Sodium Stannate	Lb.	9¾	@	10
Strontium Nitrate	Lb.	7¼	@	8
Sulphur, Roll	C.	1.85	@	2.15
Sulphur, Flowers	C.	2.20	@	2.60
Sulphuric Acid, 60° B	C.	85	@	1.00
Talc (American)	Ton	15.00	@	20.00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	13	@	13
Tin Oxide	Lb.	49	@	51
Tin Chloride (36°)	Lb.	11	@	11½
Zinc Chloride (granulated)	Lb.	4¼	@	4½
Zinc Sulphate	Lb.	2¼	@	2½

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	40	@	45
Black Mineral Oil, 29 Gravity	Gal.	12	@	12½
Castor Oil (No. 3)	Lb.	9½	@	11
Ceresin (yellow)	Lb.	9	@	20
Corn Oil	C.	5.95	@	6.00
Cottonseed Oil (crude), f. o. b. mill	Gal.	31½	@	33
Cylinder Oil (light, filtered)	Gal.	19½	@	20
Japan Wax	Lb.	8½	@	9
Lard Oil (prime winter)	Gal.	75	@	83
Linseed Oil (double-boiled)	Gal.	74	@	88
Paraffine Oil (high viscosity)	Gal.	23½	@	24
Paraffine (crude 120 @ 122 m. p.)	Lb.	3	@	3⅛
Rosin Oil (first run)	Gal.	36	@	50
Spindle Oil, No. 1	Gal.	14	@	14½
Sperm Oil (bleached winter) 38°	Gal.	76	@	78
Stearic Acid (double-pressed)	Lb.	10¼	@	10½
Tallow (acidless)	Gal.	63	@	65
Tar Oil (distilled)	Gal.	30	@	31

METALS.

Aluminum [No. 1 ingots]	Lb.	18⅝	@	19
Antimony (Hallet's)	Lb.	7⅜	@	7⅝
Bismuth (London)	Lb.	—	@	1.80
Copper (electrolytic)	Lb.	13.08	@	13.15c
Copper (lake)	Lb.	13.2	@	13.35c
Lead, N. Y.	Lb.	—	@	4.45c
Nickel	Lb.	40	@	50
Platinum (refined)	Oz.	48.50	@	49.00
Silver	Oz.	54	@	56
Tin	Lb.	—	@	44⅛
Zinc	Lb.	6.22	@	6.37½c

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume IV | FEBRUARY, 1912 | No. 2

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Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered at the Post-Office, Easton, Pa., as Second-class Matter.

TABLE OF CONTENTS.

EDITORIALS:

Potash from the Pacific Kelps 76
Surface Combustion 77
Physical-Industrial Chemistry 79

ORIGINAL PAPERS:

Some Problems in Chemical Engineering Practice. Manufacture and Testing of Shipping Cylinders for Anhydrous Ammonia. By F. W. Frerichs 80
The Manufacture and Testing of Carbonic Acid Cylinders. By John C. Minor, Jr. 88
The Composition of Some Mine Gases, and a Description of a Simple Methane Apparatus. By G. A. Burrell 96
Salt-Rising Bread and Some Comparisons with Bread Made with Yeast. By Henry A. Kohman 100
A Study of the Viscosity of Fish Oils. By George F. White 106

LABORATORY AND PLANT:

Hardness of Plasters and Cements, and a Simple Chronographic Apparatus for Recording Set. By Chas. F. McKenna 110
Recent Improvements in Filtration Methods. By Ernst J. Sweetland 114
An Electric Still Adapted for Difficult Distillations. By I. C. Allen and W. A. Jacobs 118
The Carbon Dioxide Recorder as a Factor in Fuel Economy. By E. A. Uehling 123

ADDRESSES:

Mineral Wastes: The Chemists' Opportunity 125

PERKIN MEDAL AWARD:

Introduction. By M. C. Whitaker 131
Presentation Address. By C. F. Chandler 132
Address of Acceptance. By Herman Frasch 134
Geology of the Sulphur and Sulphur Oil Deposits of the Coastal Plain. By Captain A. F. Lucas 140
Sulphur Mines of the Union Sulphur Company in Louisiana. By F. H. Pough 143

SCIENTIFIC SOCIETIES:

Forty-fifth Annual Meeting A. C. S. Program of Papers 147
Minutes of Division of Industrial Chemists and Chemical Engineers 148
Minutes of Division of Agriculture and Food Chemistry 149
Minutes of the Division of Pharmaceutical Chemistry 150
Minutes of Meeting of Fertilizer Division 151
Minutes of the Meeting of the Rubber Section 152

NOTES AND CORRESPONDENCE:

Note on the Production of Mercury Fulminate. By Charles E. Munroe 152
Tungsten Production in the United States in 1911 153
Clay Products in 1910 153
Lead Industry in 1910 153

CONSULAR AND TRADE NOTES:

German Potash Interests 154
Norwegian Guano Shipments to United States 154
Glass Paving Blocks in France 154
Palm-Oil Industry of West Africa 154
Increased Customs Duties in Bolivia 154

BOOK REVIEWS:

Addresses to Engineering Students; Die Polarimetric der Erdöle 155

NEW PUBLICATIONS 156
RECENT INVENTIONS 157
MARKET REPORT 158

EDITORIALS

POTASH FROM THE PACIFIC KELPS.

During the spring and early summer of 1911, systematic work was inaugurated to determine the fertilizer resources of the United States. Sources of supply for phosphoric and nitrogenous fertilizers were more or less well known. There was no known source of potash salts, however, of any economic importance. It is obviously desirable that such a source should be found and developed, and this fact was accentuated by the controversies arising between the "Kali Syndicate" and certain American importers which received much notice in the current press and was the occasion of animated diplomatic exchanges between the Governments of the parties to the controversy. The resources of the United States in possible sources of "potash" therefore received special attention, and various lines of inquiry were actively prosecuted. One of these, so far, has yielded positive results. (For a complete description of this work see Senate Document 190, Sixty-second Congress, 2nd session, entitled "A Preliminary Report on the Fertilizer Resources of the United States.") Balch (THIS JOURNAL, 1, 777 (1909) has called attention to the giant kelps of the California coast as occurring in enormous quantities and being especially rich in potash salt. Samples of the kelp from Southern California and the salts derived therefrom were submitted to this office by Mr. Balch in September, 1910, and further data were secured from various sources.

Early in the summer, three field parties were organized: Prof. George B. Rigg observed and mapped the kelp beds or groves in about a half of Puget Sound; Prof. Frank M. McFarland surveyed the groves from San Francisco Bay to Point Sur; and Captain W. C. Crandall, of the La Jolla Station of the Marine Biological Association of San Diego, surveyed the groves of the main shore and outlying islands from Point Loma to Point Conception. Officers of the Bureau of Fisheries made still further observations regarding the kelps of Alaska.

In the work this summer something over one hundred square miles of kelp groves were surveyed, and there is reason to believe that the total area on the Pacific Coast, from Magdalena Bay to Shumagin Islands, may possibly be 6 or 8 times this. Quite a large number of kelp and rockweeds were found, although generally the larger groves are approximately "pure stands." Two of the kelps are chiefly of importance as sources of potash. In the northern groves the important kelp is the *Nereocystis luetkeana* and in the southern groves it is the *Macrocystis pyrifera*. From Point Sur southward this latter occurs in large groves sometimes several square miles in area, and often in very dense masses.

Nereocystis grows in almost any depth of water, where there is a rocky bottom and also a strong tideway or otherwise continual movement of the water. Macrocystis grows only on exposed coasts where there is much movement of water, and practically always at depths of from 6–10 fathoms. As the carbon dioxide and the oxygen necessary to the metabolism of the plant must be obtained from the dissolved gases in the water a continually renewed mass of water must be available. This fact, probably, accounts for the difficulties encountered in trying to artificially propagate these algae under laboratory of aquaria conditions. A rocky bottom is essential for the holdfasts which these plants have in lieu of roots, and to anchor them.

Nereocystis is an annual. The fruiting season is about over by the middle of July, and in order to maintain the groves this algae should not be cut before that time. Macrocystis, however, is probably a perennial; at least, its life is more than a calendar year, and if cut early in the summer, it is said to be able to regain its luxuriant growth in 40 days or thereabout. At least two cuttings, therefore, should be practicable. Its habit of growth, moreover, the spores forming on fronds well below the surface, tends to provide against its extinction or serious depletion. Nevertheless, it would probably be wise to maintain a "closed season" for this algae also and not permit more than two cuttings per season, thus insuring a sufficient fruiting to maintain the groves unimpaired. Some form of governmental protection or control of the groves is obviously necessary to their maintenance and efficiency.

The cutting and harvesting of the kelp is a detail of the industry which is in a far from satisfactory shape. Several forms of cutters have been suggested and a few tried. This is, however, a mechanical detail which American ingenuity will unquestionably settle soon now that it has been shown to be worth while. It probably wil not be practicable to cut the kelp more than 10 or 12 feet below the surface of the water, and in the case of the Macrocystis at least a greater depth of cutting should not be permitted, in order to insure fruiting and reseeding of the groves.

Kelp was originally a term applied to the ashes of seaweeds and rockweed, but has become, especially in this country, synonymous with the seaweeds or brown floating algae, and on the Pacific Coast is applied popularly to the two plants cited above. These plants among other characteristics have this in common, they absorb relatively large amounts of potassium chloride from the sea water, much larger than most other algae either of the Pacific or other waters. Dr. J. W. Turrentine has made a large number of analyses. From his data it appears that Nereocystis contains about 30 per cent. of its dry weight of potassium chloride and Macrocystis nearly as much. With both kelps, as they dry out, large quantities of potassium chloride, mixed with varying amounts of other salts,

effloresce on the surface, and can be removed readily by simply shaking. Practically all the potassium salts can be obtained by lixiviation of the dried plant or of its ash.

Neither Nereocystis nor Macrocystis of the Pacific littoral contain as much iodine as many other seaweeds and rockweeds. Nevertheless, the amounts present are notable and contrary to popular belief; the southern kelp contains more than does the northern.

According to Turrentine's analyses Nereocystis contains about 0.16 per cent. and Macrocystis about twice as much. Besides iodine, other useful products can be obtained from these kelp, of which, however, space will not permit a discussion here.

It is not possible as yet to give an accurate estimate of the amount of potassium chloride which the Pacific kelp groves can yield annually. With all conditions at their best the maximum possible yield might be in the neighborhood of 8 million tons, worth at present prices about $300,000,000. No such yield is probable, however, at least in the near future. Taking every consideration, and leaning strongly to conservatism it may be said that it ought to be perfectly practicable to obtain an annual yield of at least a million tons of potassium chloride, worth at present prices upwards of $30,000,000. The iodine obtainable at the same time should go far toward paying the expenses of harvesting the kelp and extracting the potash.

It has been assumed in some quarters that because the kelp can be made to yield about three times the present total potash importations from Germany the latter will be stopped or greatly diminished. This is very much to be doubted. Existing business engagements will ensure continued importation for some years to come. It is possible, and greatly to be desired, that potash from American kelp will reduce the price of potash salts. But the vast bulk of the potash salts goes into the South Atlantic States because these states at present are the great fertilizer consumers. Inevitably the Trans Mississippi States must soon use fertilizers and in fact the movement has already begun. A very large increase in the consumption of fertilizers, and therefore of potash, may be anticipated within the next few years, enough probably to take up the American production in sight and the importation to be obtained from Germany as well.

The great importance of the kelps lies not in the probability of their excluding German potash, but (1) if properly managed, in preventing a monopoly and regulating prices; (2) in making possible a greatly extended use of fertilizers, and thereby perhaps even stimulating importations; and (3) in times of stress, giving the country a resource and preventing the agricultural interests from being at the mercy of an outside power.

F. K. CAMERON.

SURFACE COMBUSTION.

In view of the wide-spread publicity given to the lecture of Professor W. A. Bone, of Leeds, before the American Gas Institute at St. Louis and the Chemsits' Club in New York, October, and especially in view of the general acceptance by gas engineers and chemists in general of his process as a new discovery in combustion, it seems highly desirable to present a brief review of this art. Professor Bone's demonstrations were all concerned with the burning of explosive gaseous mixtures continuously by method which (quoting)

"consists essentially in injecting, through a suitable orifice at a speed greater than the velocity of back firing, an explosive mixture of gas (or vapor) and air in their combining proportions into a bed of incandescent, granular refractory material, which is disposed around or in proximity to the body to be heated."

This method of burning explosive gaseous mixtures was used by C. E. Lucke, in 1900, or about eleven years ago. It was made the subject of a long series of experiments, the results of which were published in a paper entitled "The Heat Engine Problem," presented to the American Society of Mechanical Engineers, December, 1901, and forming part of his Doctor's Dissertation, from which the following is quoted:

"The desirability of being able to burn an explosive mixture continuously and non-explosively under commercial rather than laboratory conditions having been long obvious, a series of experiments was undertaken at Columbia University with this end in view. Many experiments were made and various results obtained, but as a full account would take too much space and avail little, only a few characteristic experiments will be noted as leading up to the result. Consider a mass of explosive mixture passing through a non-conducting tube with a uniform velocity, v. Then, if inflammation be started at some point, the surface of combustion may remain at rest or move with or against the current. Denote the rate of propagation by r. Then, when v is greater than r the surface of combustion will move with the current, and if the tube has an end, the flame will 'blow off' and combustion cease; if $v = r$ the surface of combustion will remain at rest, other influences being inoperative; if v is less than r, the surface of combustion will move back toward the source, or 'back flash.'" "In a practicable system of burning an explosive mixture continuously, we may state the following as desiderata and later see how they can be secured.

I. 'Back flashing' must be prevented.

II. 'Blow off' must be prevented.

III. Combustion surface must be localized.

IV. It must remain localized for wide ranges of feed or velocity of flow of the mixture.

V. The localization must be unaffected by changes of temperature.

VI. Large or small quantities must be burned without affecting the above, and the transition from very small quantities to very large, or *vice versa*, however sudden, should be easy.

The first requirement might be accomplished in three ways:

(*a*) By using a long tube of some conducting material and so small in diameter as to prevent the passage of the flame-cap under any circumstances.

(*b*) By using wire gauze screens.

(*c*) By causing the mixture to flow at some point with a velocity always greater than the rate of propagation.

The first (*a*) is impracticable, as it permits of only small quantities being burned; the second (*b*) will not work when the wire gauze gets hot; this leaves (*c*) which is practicable."

"Hence we must put down as the first requirement in our desired method of combustion the following: *At some point before the combustion surface is reached the velocity of feed must be such that v is greater than r.*

Requirement II might be accomplished in three ways:

(*a*) By so reducing the velocity after passing the high speed point that we have at some surface $v = r$.

(*b*) By suddenly increasing the temperature of the mixture so as to increase the rate of propagation while v remains constant; or

(*c*) By reducing v, by spreading the current, and increasing r by heating. All of these ways are practicable; but, as a reduction of velocity alone or a sufficient heating alone would not produce the desired results so well as both operating together, there was introduced as the second requirement in our desired method, the following: *After passing the point where v is greater than r, the velocity of the mixture should be so reduced and its temperature increased as to make* $v^1 = r^1$."

"Many ways of bringing about the above were tried, but only one seemed preeminently good by reason of its simplicity and effectiveness, for it fulfils most perfectly the requirements proposed for our desired method; this is, to fill a cone with fragments of refractory material such as pottery, broken crucibles, bits of magnesite, or any other rock that will stand the high temperature without fusing. In cones of 60 degrees, and with a $^1/_4$-inch orifice, I have ound pieces of about $^3/_8$ inch diameter to answer well. These separate pieces of solid matter interpose many reflecting surfaces without materially hindering the advance of the mixture, and cause it to spread in the way desired, keeping the surface of combustion spherical and preventing diffusion. A variation of velocity causes the spherical surface of combustion to vary only in diameter, and the limits of feed are determined only by the size of the cone."

"A cone of given altitude will give the greatest range of variation of diameter of cross section when its angle is 180 degrees. This is a plane surface which, with the orifice and broken rock should appear as in Fig. . (Fig. 49, page 58, 'The Heat Engine Problem'). Here the surface of combustion is approximately a semi-sphere. Trial shows that this arrangement

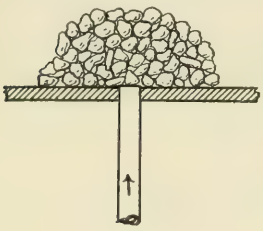


Fig. 1.

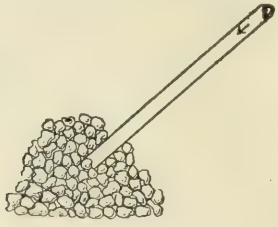


Fig. 2.

works perfectly, and the limits of feed are determined only by the size of the pile of rock surrounding the opening. A cone of 360 degrees, or no cone at all suggest the surrounding of the nozzle by broken rock without any enclosing walls Fig 2 (Fig. 50, page 58, 'The Heat Engine Problem'). This arrangement also works remarkably well. The surface of combustion is here approximately a sphere giving the greatest possible increase in area of the surface of combustion for the distance traveled from the nozzle."

"Not only is the greatest possible range of action by velocity reduction thus obtained, enabling the greatest possible amount of mixture to be burned in a given volume, but this amount is further *augmented by reason of the increase of the rate of propagation caused by the passage of the mixture between the hot fragments.* Hence both principles operate simultaneously toward the desired end."

"We have thus arrived at a method of continuously burning explosive mixtures of all sorts, whether in the chemical proportion or not."

"When a chemical proportion is maintained in the mixture, all the combustion takes place on the combustion surface, giving absolutely neutral products of combustion, but when an excess of gas is present within certain limits, all gas that can find oxygen burns explosively between the solids, while the excess acts merely as a neutral diluent to be burned when it meets an oxygen atmosphere later on. By properly placing the oxygen atmosphere to burn the excess gas, we can get the hot products either reducing or oxidizing—reducing after leaving the explosive combustion surface and before meeting the excess of oxygen in the atmosphere, oxidizing after that meeting."

This quotation is reproduced, together with other similar matter by Hutton in his book "The Gas Engine," 1903, pages 486–493. It cannot, therefore, be said that the scientific and technical world has not had opportunity enough to become acquainted

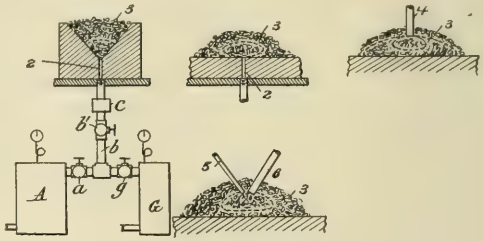


Fig. 3.

with this work, done some eleven years ago and in print for ten years, especially as many journals quoted portions of the A. S. M. E. paper, mentioned above, as well as quotations from another paper by the same author, presented to the A. S. M. E., May, 1902, on the application of the same process to the burning of oils.

Not only does it appear from the above that Lucke practiced this process for both gases and oils prior to 1901, but two patents were issued to him for the process. U. S. No. 755,376 and No. 755,377, filed respectively June 7, 1901, and July 30, 1901, both issuing March 22, 1904, contain illustrations and descriptions of apparatus substantially the same as used by Bone, but the claims cover the *method* broadly and are not confined to the apparatus shown. To make clear the comparison, consider Figs. 3 and 4, which are reproductions of the patent illustrations,

with Fig. 5, reproduced from the *American Gas Light Journal*, illustrating Bone's Apparatus (Dec. 4, 1911). The following quotations of the patent claims will show the scope of these two patents in

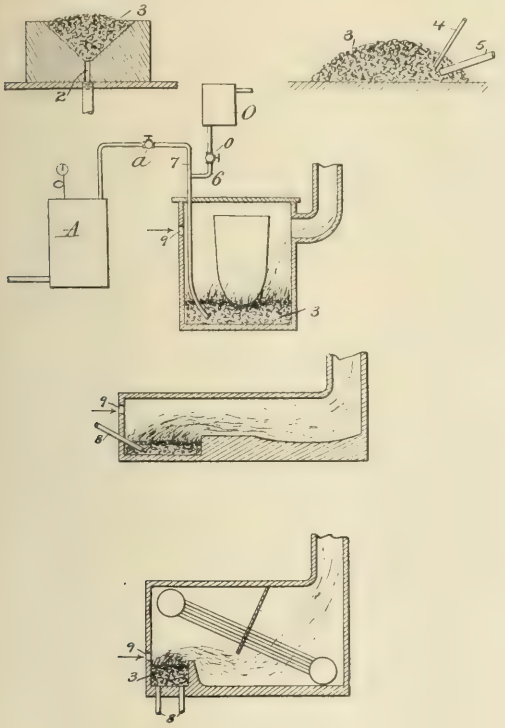


Fig. 4.

general though only the first claim in each case is quoted, there being three claims for the first patent and five for the second.

CLAIM 1, U. S. PATENT NO. 755,376 TO LUCKE.

"The method of burning explosive gaseous mixtures which consists in causing the mixture to move with a velocity greater than the rate of propagation of inflammation through the mixture, and then reducing the velocity to the rate of propagation of the inflammation and preventing diffusion with other gas, by causing the mixture to spread out so that the successive surfaces of uniform velocity shall have adjacent points in any such surface at substantially the same distance from the place where spreading begins, and burning the mixture at the surface at which the velocity is equal to the rate of propagation of inflammation, substantially as described."

CLAIM 1, U. S. PATENT NO. 755,377 TO LUCKE.

"The method of burning fluid fuel which consists in causing the fuel and a suitable combustion-supporting gas in proportions such that there will be an excess of fuel over the quantity required for perfect chemical combination with the oxygen of the supporting-gas to flow into a hot combustion-bed, the supporting-gas moving with such velocity as to cause the resulting mixture to move with a velocity greater than the rate of propagation of inflammation through the mixture, and the combustion-bed being of such a nature as to cause the mixture to spread out so that the successive surface of uniform velocity shall have adjacent points in any such surface at substantially the same distance from the place where the spreading begins, thereby reducing the velocity of the mixture to the rate of propagation of inflammation and preventing diffusion with other gas; and burning within the bed so much of the fuel as herein forms with the supplied oxygen an explosive gaseous mixture and burning at or beyond the surface of the bed the remainder of the fuel, substantially as described."

It would appear that these two claims of the method of burning explosive mixtures whether in chemically combining proportions or not, as used by Bone, are broadly covered and allowed.

It is of interest in this connection to quote the U. S. Patent Office citations which were overcome in connection with the Lucke cases, and these are: 1, Verstraet, Jan. 12, 1869; 2, Smith, No. 170,198, Nov. 23, 1875; 3, Paquelin, No. 180,155, July 25, 1876; 4, Weeks, Oct. 12, 1880; 5, Hubbard, No. 260,983, July 11, 1882; 6, Wainwright, Oct. 12, 1886; 7, Grant, No. 457,081, Aug. 4, 1891; 8, Rogers, March

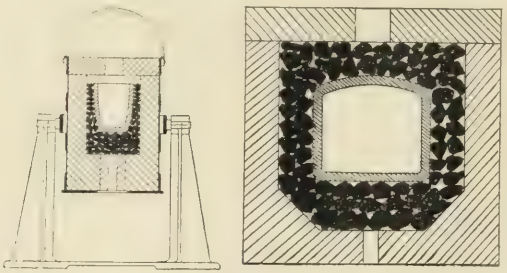


Fig 5

22, 1892; 9, Archer, Feb. 28, 1893; 10, Ladd, No. 550,831, Dec. 3, 1895; 11, Barker, No. 577,638, Feb. 23, 1897; 12, Burrows & Weaver, No. 672,888, April 30, 1901; Musker & Hay, No. 676,096, June 11, 1901. Detailed examination of the Bone paper reveals only one structure or apparatus not used or specifically described by Lucke, and that is the porous diaphragm in place of the broken refractory material. There appears to be, however, no essential difference between a porous diaphragm and a body of broken material except in the shape or size of the passageways open to the flow of the gaseous mixtures.

In view of these experiments, the wide-spread and apparently general acceptance of the supposition that Bone's work is new seems difficult to support. Apparently, the only journal that has not fallen into this error is "*Power*" which in its issue of Nov. 21, 1911, calls attention to the similarity of Lucke's and Bone's processes, editorially.

PHYSICAL-INDUSTRIAL CHEMISTRY.

At first sight it seems as though the two divisions of organic chemistry and inorganic chemistry covered the whole field and as though a man who was well posted in these subjects would have all the knowledge of pure chemistry needed by one going into industrial chemistry. This is not true because the organic chemist and the inorganic chemist of the colleges

are interested primarily in the nature of the final product, while the technical man is much more concerned with efficiency in its bearing on cost of production. Consequently it is being recognized more clearly every year that a thorough grounding in organic and inorganic chemistry is merely a preliminary stage in the training of an industrial chemist and that his chemical course is incomplete unless it leads up to and includes *physical chemistry*, which means the common-sense study of methods. Some fifteen years ago I announced at one of the meetings of the American Chemical Society that a proper training in physical chemistry was the best possible training for a man going into technical work. At the time the statement was considered as the unfortunate outburst of a misguided and unbridled imagination. To-day it is such a truism that it is out of place anywhere except in an editorial.

This is the more interesting because the real development has scarcely begun. Within the next three or four years we shall get colloid chemistry on a sound scientific basis, and when that time comes the field of the physical chemist will include: photography; tanning; brewing; rubber; dyeing; soap; textiles; artificial silk and other filaments; cellulose; paper; celluloid and other plastics; starch; glues and cements; paints, lacquers and varnishes; lubricating oils and greases; clay, fuller's earth and putty; inks; ceramics; glass and enamels; milk, butter and caseine; cooking; water purification and sewage disposal; food preservatives; slags; soils; physiology, biology and medicine.

WILDER D. BANCROFT.

ORIGINAL PAPERS

SOME PROBLEMS IN CHEMICAL ENGINEERING PRACTICE.[1]

MANUFACTURE AND TESTING OF SHIPPING CYLINDERS FOR ANHYDROUS AMMONIA.

By F. W. FRERICHS.

Received January 5, 1912.

INTRODUCTION.

Encouraged by some of my friends, I offer to-day what may be called a continuation of the address which I delivered in Chicago, six months ago, and which has been already published in the October and November (1911) issues of THIS JOURNAL.

For to-day, I have selected three problems in chemical engineering practice, the characters of which are widely different from the previous problems and which give additional proof of the statement that the field of chemical engineering is exceedingly varied and difficult to define. Again, these problems are selected with a view of giving, to the student of chemical engineering, an idea of the variety of questions with which he may be confronted but, at the same time, they are chosen to call attention to the wide difference between scientific chemical research and the investigation of chemical engineering problems.

Scientific research treats principally with reactions which produce definite substances and can be followed up by chemical formulae.

Chemical engineering problems are based on reactions also but they include cost, quality, yield, labor and safety of those engaged in the manufacture of goods, and provide for the convenience in handling the goods by the consumer. In the manufacture of chloroform from bleaching-powder and ethyl alcohol, the process was known, but the object of the research was to find the conditions under which the maximum yield could be obtained by a known reaction and to construct apparatus which would give these conditions with greatest economy. In the construction of laboratory apparatus referred to, the saving of time effected by the improved apparatus was the leading element. In the manufacture and testing of shipping cylinders for liquefied ammonia gas, the safety of handling and the convenience to the consumer was the object of investigation.

These, together with the three problems treated, give only a few forms of the great variety of demands which are likely to be made on the chemical engineer, and I should feel highly gratified if I have given an incentive to others of our members to follow in this direction, by giving the solution of additional cases, so that we may obtain a large variety of solved problems by which the students in our profession may be guided in their work.

MANUFACTURE AND TESTING OF SHIPPING CYLINDERS FOR ANHYDROUS AMMONIA.

All chemical manufacturers produce goods and these goods need packages in order to be marketed. The question of packages is often more difficult and requires more study and capital than the manufacture of the goods to be shipped in them and this is particularly the case if the packages are intended for compressed or liquefied gases, which can only be handled with reasonable safety if the containers in which the gases are confined are constructed and kept in such a manner, that danger in handling them as far as practicable is excluded.

It is often said that the manufacture of packages is not a chemical problem, and chemists should not meddle with questions outside of their line; that if questions of packages arise they should go to men who make them and take their advice. But there are instances in which the chemical engineer is confronted with the necessity of going himself into the manufacture of containers, and in such cases the manufacture of packages becomes a chemical engineering problem. I experienced a case of that kind not long ago when I needed a large number of valves for ammonia shipping cylinders, and since the object

[1] Address read at the Annual Meeting of the American Institute of Chemical Engineers, in Washington, D. C., December 20, 1911.

involved many thousands of dollars I went to the trouble of studying the question thoroughly.

I made designs and had models made at great expense, some of which you see among the exhibits.

When I had arrived at a model which seemed to fill my requirements, represented by Fig. 1, I selected a shop where similar work had been done and contracted at their price for 1,500 valves, equal to model submitted. When deliveries were begun I had to reject every valve. When the defects were pointed out it was admitted that the differences were there, but it was contended that the valves delivered were just as good and answered the purpose. To this I took exception. As the proprietors of the shop were desirous of fulfilling their contract, I went into their shop to help things along, and investigated the cause of the unsatisfactory work which had been delivered.

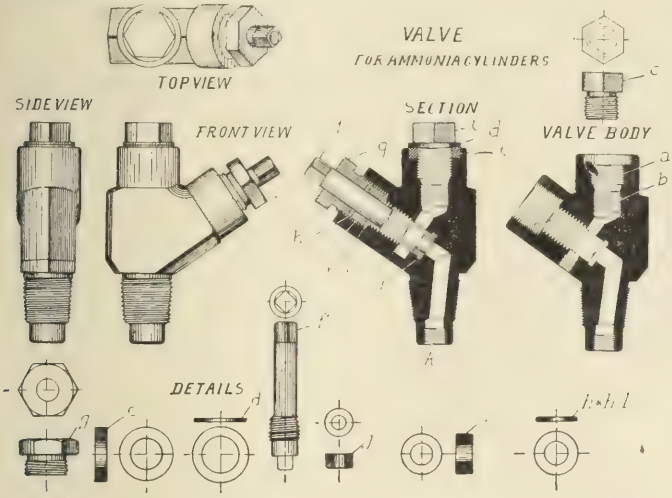


Fig. 1.—*a*, 1/2" pipe connection; *b*, 3/8" pipe connection: *c*, plug: *d*, iron washer; *e*, rubber washer; *f*, valve stem; *g*, stuffing box nut or gland; *h*, and *h*¹, iron washers; *i*, packing; *j*, soft metal seat; *k*, pipe connection for dipper pipe.

The drop forgings for the valve bodies were made by a reliable firm on my direct order. There was no trouble on this account and the valve stems and the nuts were made from standard steel bars, so that there could not be any fault with the material.

In the shop I found some good and some worn machine tools, and there were some good machinists, but the majority of help were second-class men. Since work was continuously coming in it was necessary to shift my work from one place to another to keep the shop going, and the result was unsatisfactory work.

The valve stems and lock nuts had been sublet to another shop of good reputation at a contract price, but they were turned out on a much used screw machine, were therefore not accurately made, and were not satisfactory to me.

For making good valves, perfect tools and good mechanics seemed to be necessary, and in order to turn them out at the rate of about 200 valves per week, by my calculation, a sum of about $3,000 was to be invested in tools. The shop was unwilling to make such an investment. Neither could they promise to put only first-class machinists on the work, unless I would agree to pay a price which was prohibitive.

In this manner, I was forced to undertake the work myself. I bought the best machine tools I could obtain, and arranged a shop containing two screw machines, two lathes, two drill presses, and one gas furnace for case-hardening. Furthermore, one power hack saw and emery wheel, all of which cost about $3,000. I employed three good machinsits and two helpers, put one of my engineers in charge of the shop and turned out 180 good valves per week at a cost which was much less than the price, which I had paid to the outside shop for unsatisfactory work.

Compressed and liquefied gases are manufactured in very large quantities, and for their safe transportation by common carriers, rules have been adopted in many countries for constructing and testing containers in which they may be accepted for shipment by transportation companies.

Containers used for this purpose generally have the form of cylinders.

One set of rules has been agreed upon by the railroads of Germany, Austria Hungary, Belgium, France, Denmark, Italy, Luxembourg, The Netherlands, Roumania, Russia, Sweden, and Switzerland, which rules are commonly referred to as the International Rules for European countries. Up to recent times there were, however, no regulations of this kind in the United States but the American Railroad Association, in conjunction with committees appointed by manufacturers of compressed gases, have been working on such rules for several years, and these rules were recently adopted by the Interstate Commerce Commission of the United States, and went into effect, October 1, 1911.

The general rules, applying now to shipping containers for compressed and liquefied gases, are as follows:

"(*a*) Gases that may combine chemically must not be shipped in one cylinder. Cylinders purchased hereafter for the shipment of compressed gases must be made in accordance with specifications approved by the Interstate Commerce Commission.

"(*b*) By water jacket, or other suitable tests, each cylinder used for shipping liquefied gases must be subjected at least once in five years to a uniform interior pressure not less than one and one-quarter times the interior pressure that would result from heating the cylinder uniformly, in its maximum charged condition, to a temperature of 130° F. Each cylinder used for shipping under pressure not exceeding 1,000 pounds per square inch nonliquefied gases or gases in solution, must be subjected at least

once in five years to a uniform interior pressure not less than twice the charging pressure for such cylinder, corresponding to a temperature of 70° F.; when the charging pressure exceeds 1,000 pounds per square inch, the test pressure must not be less than one and one-half times the charging pressure. A cylinder must be condemned when it leaks, when the permanent expansion is due to local weakness, or when it is uniform and exceeds 5 per cent. of the total expansion. When the charging pressure is less than 300 pounds per square inch it will not be necessary to measure the permanent expansion in quintennial pressure tests, provided the cylinder in question has previously passed this test.

"(*c*) The weight of gas charged into any cylinder must not at a temperature of 130° F. cause an interior pressure in excess of three-fourths of the elastic limit of the weakest part of the cylinder.

"(*d*) The manufacturer must not offer for transportation a cylinder filled with such charging density of any gas as would produce failure in the test prescribed for that gas.

"(*e*) After December 31, 1914, all cylinders must plainly be stamped with the date of last test—for example, '4–09' for April, 1909—or otherwise durably marked to show compliance with this rule; and by December 31, 1911, not less than one-fourth of the cylinders in use for shipping purposes must be thus tested and marked.

"(*f*) Cylinders containing acetylene gas must be made of tough steel and must be completely filled with a porous material that has been tested by the Bureau of Explosives and approved by the Interstate Commerce Commision, and this material must be charged with acetone or its equivalent not to exceed 40 per cent. of the interior volume capacity of the cylinder. The pressure in cylinders containing acetylene gas must not exceed 250 pounds per square inch at a temperature of 70° F."

In addition to these general rules, specifications for shipping containers are adopted, each set of specifications being different for different gases.

1. The specifications for lap-welded cylinders intended for shipping anhydrous ammonia are shown in Table I.

2. Cylinders must be manufactured from lap-welded pipe made of soft steel of the best welding quality, free from blisters, cracks, or other injurious defects.

INSPECTION AND TESTING OF MATERIAL.

3. The pipe intended for these cylinders must be manufactured by the best appliances and according to the best modern practice, each length to be inspected separately for defects inside and outside and then subjected to the following tests:

(*a*) To each crop end cut from the pipe from which the cylinders are to be made, a flattening test must be applied with the weld 45° away from the side which is subject to the greatest bending stress, with knife edges of wedge shape converging at an angle of 60°, the point being rounded off with a radius of one-half inch. In this test, the crushing of the walls must be to within four times the thickness of the metal, and a crop end must withstand the test without cracking.

(*b*) An internal hydrostatic test of 600 pounds per square inch must be applied to each length of pipe under which it must not show signs of leaking at the weld or elsewhere.

4. Each finished cylinder must be tested by internal hydrostatic pressure as specified in above table, paragraph 1, the test to be conducted as follows:

(*a*) After filling cylinder with water, the test pressure specified must be applied for the purpose of detecting leaks and rounding up the cylinder.

(*b*) The cylinder, if tight, must be placed in a water jacket or other approved apparatus for measuring the expansion, and the test pressure again applied. The permanent expansion under this test must not exceed 10 per cent. of the whole volumetric expansion at the pressure specified.

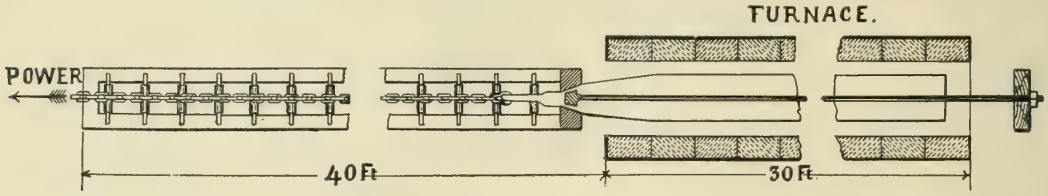


Fig. 2.

GENERAL CONSTRUCTION AND INSPECTION.

5. The manufacture of the cylinders must be completed with the best appliances and according to the best modern methods. All finished cylinders must show a reasonably smooth surface, and must have passed the above inspection and tests without showing any defect in workmanship or material likely to result in any appreciable weakness in the finished cylinder. Each completed cylinder must be inspected for such defects at the mill by the purchaser or his representatives before acceptance.

These rules and specifications are the results of extensive tests made with cylinders taken from the present equipment of the various manufacturers and with new cylinders made for the specific purpose of testing.

I am much pleased to say right here that tests have shown the shipping cylinders of old equipment generally to be of greater strengths than required by the regulations, from which fact it may be concluded that manufacturers always have been anxious to make shipping cylinders of ample strengths so that accidents might be prevented.

TABLE I.—SHIPPING CONTAINER SPECIFICATION NO. 4.—(See par. 1822(a), p. 41.)

Lapwelded Steel Cylinders for Anhydrous Ammonia.
Revised January 1, 1912. Effective March 31, 1912.
Table of Details as to Dimensions.

Outside diameter of cylinder.	Over-all length of cylinder.		Nominal thickness of cylinder wall.	Test pressure per square inch.	Head.			Mouth.			Weight of cylinder.	
					Depth.	Low limit	High limit.	Diameter.	Low limit.	High limit.	Low limit.	High limit.
Inches.	Ft.	in.	Inch.	Pounds.	Inches.	Inches	Inches.	Inches.	Inches.	Inches.	Pounds.	Pounds.
10	3	10	0.19	1000	3 3/4	3 9/16	3 15/16	7 1/2	7 3/8	7 5/8	87	112
10	4	0	0.19	1000	3 3/4	3 9/16	3 15/16	7 1/2	7 3/8	7 5/8	90	115
10	7	0	0.19	1000	3 3/4	3 9/16	3 15/16	7 1/2	7 3/8	7 5/8	150	175
10	3	10	0.27	1500	3 3/4	3 9/16	3 15/16	7 1/2	7 3/8	7 5/8	113	141
10	4	0	0.27	1500	3 3/4	3 9/16	3 15/16	7 1/2	7 3/8	7 5/8	117	145
10	7	0	0.27	1500	3 3/4	3 9/16	3 15/16	7 1/2	7 3/8	7 5/8	203	237
12	7	0	0.21	1000	3 3/4	3 9/16	3 15/16	9	9	9 1/4	220	250

By these regulations, containers for liquefied gases must be safe at pressures to which the fully charged cylinders will be exposed at 130° F. and the following table gives the pressures corresponding to various temperatures for some liquefied gases most commonly handled.

TABLE II.
Test pressure, absolute.

	Absolute pressure at			Inter-					Critical temperature.	
				American rules.	national and German rules.		Critical pressure absolute.			
	15° C. 59° F.	38° C. 100° F.	55° C. 130° F.	Lbs.	Lbs.	Atm.	Lbs.	Atm.	°C.	°F.
Carbon dioxide	768	1160	1227	2454	2793	190	1132	77	31.1	88
Nitrous oxide.	732	1112	1180	2360	2646	180	1103	75	35.4	96
Ammonia.....	104	215	340	425	441	30	1690	115	130.0	266
Chlorine.....	85	156	250	312	323	22	1374	93.5	145.4	294
Sulphur dioxide	40	..	147	184	176	12	1160	78.9	155.4	312

From this table it is seen that the pressures vary greatly with the different gases and, consequently, shipping cylinders used for different gases must be of different strengths

From the table it is also evident that, in a general way, the International and American Rules agree fairly well, and we will now have to see in which way the shipping cylinders must be constructed in order to comply at the same time with the rules of the Railroad Companies which are considered by them necessary to secure safe handling; with the interests of the mills, which require that the specifications be inside of the possibility of manufacture at a minimum cost; and with the interests of manufacturers and consumers of the goods, which make it desirable that the shipping cylinders be as light as possible in order to facilitate the handling and securing the lowest freights.

In designing shipping cylinders, the first question is: which metal can be used and what must be the strength and thickness of the material of the container to withstand the pressure to which the cylinder will be subjected?

The answer to this question is found by the following considerations:

Materials used for construction of shipping cylinders must be indifferent to the gases, which are to be shipped in them.

All materials have constant properties, among them, ductility, the tensile or breaking strength and elastic limit.

A bar of any material, having a cross section of one square inch, subjected to a moderate strain, will elongate and spring back to its initial length when the strain is released. This indicates the elasticity of the material. If, in repeating the experiment, the strain is increased, a point will be reached at which the bar does not spring back to its original length, and the strain at which this takes place is the elastic limit of the material. If the strain is increased beyond the elastic limit, the bar will be disrupted and the strain at which disruption takes place is the breaking strain of the material.

The toughness or ductility of a material is tested by bending a strip of it, and looking for cracks on the bend. It is accepted that a cylinder made of material which complies with this bending test will not break up into flying fragments if it explodes by influence of internal gas pressure.

From the values of the breaking strain and the elastic limit of materials, the dimensions of shipping cylinders may be computed.

In a cylinder, filled with compressed gas, the strain is twofold, namely, in the direction of the longitudinal axis of the cylinder and at right angles to this direction.

Given a cylinder of ten inches diameter, filled with

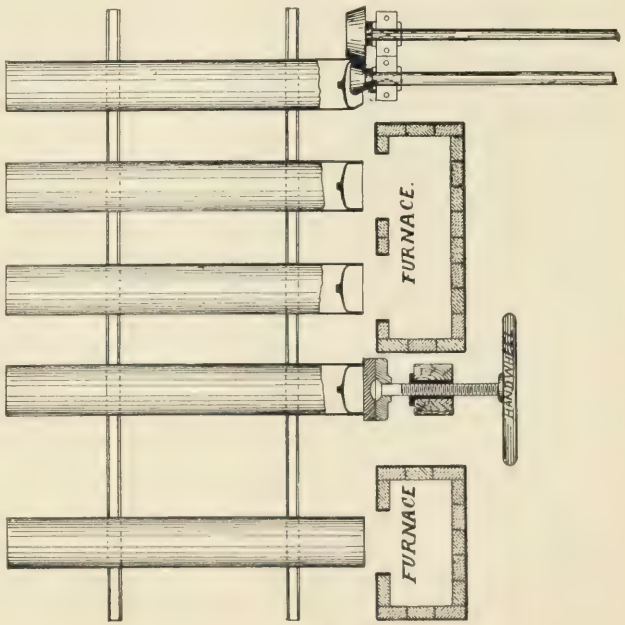


Fig. 3.

gas under 100 pounds pressure to the square inch, the total pressure on each of the circular ends is equal to the area of a ten-inch circular plane, expressed in square inches, multiplied by 100 pounds, which is equal to 7584 pounds. Since this stress must be taken up by the sides of the cylinder in the circumferencial seam, between the bottom of the cylinder and its sides, each inch of the circumference (which measures 31.4 inches) must withstand a stress of 7584 divided by 31.4, equal to 241 pounds.

Fig. 4.

The stress in the material at right angles to this direction is equal to the charging pressure on a plane which is placed through the longitudinal axis and confined by the sides of the cylinder.

Assuming again the charging pressure to be 100 pounds per square inch, then the strain on two opposite sections in the sides of the cylinder, each section one inch long and of the thickness of the material, is equal to the same pressure of 100 pounds on a plane of one inch width and in length equal to the diameter of the cylinder. This is in our case 100 times 10, equals 1000 pounds.

One-half of this stress is taken up on each of the ends of the plane or what is the same in each line of the cylindrical part of the container which is parallel to the axis of the cylinder and one inch long, which in our case is 500 pounds. This stress, being greater than the stress in the direction of the axis, it must govern in the calculation of the cylinder.

If the cylinder is made of steel and assuming the tensile strength of the material to be 50,000 pounds to the square inch, with an elastic limit of 30,000 pounds, then the tubular part of the cylinder must have a thickness, expressed in inches, equal to 500, divided by 39,000, or $^1/_{60}$ of an inch, in order to withstand an interior pressure of 100 pounds to the square inch and straining the sides not beyond the elastic limit of the material. For the heads, the required thickness of the material is the same as for the sides, if the heads have the form of a convex hemisphere. If the heads are flat or concave, the thickness is not easily figured, since it depends upon the form of the head and the bending strength of the material, which in the same material is subjected to considerable variation.

There are two kinds of pipe steel manufactured at the present time. The highest grade steel has a breaking strength of from 65,000 to 150,000 pounds, with an elastic limit of 40,000 to 110,000 pounds.

The chemical analysis of a sample of steel, having 50,000 pounds elastic limit, was carbon 0.55%, phosphorus 0.05%, sulphur 0.04%, but this steel does not weld and can be used only for the manufacture of seamless tubes.

An inferior grade of pipe steel now commonly used has a breaking strength of 50,000 to 55,000 pounds, with an elastic limit of about 30,000 pounds. Two analyses of this kind of steel have given the following results:

	S. Per cent.	P. Per cent.	Mn. Per cent.	C. Per cent.
I	0.061	0.095	50.2	0.08
II	0.068	0.121	0.42	0.08

This steel can be welded, can be bent over to four times its thickness without cracking in the bend, and furnishes at present the material for welded tubes and cylinders.

Up to about fifteen years ago manganese was not commonly used as an ingredient for pipe steel, and an increased amount of phosphorus was at that time left in the steel to give it welding qualities. Such steel has a low breaking strength of about 40,000 to 45,000 pounds, with a comparative high elastic limit of about 30,000 pounds. Two analyses of this steel have given the following results:

	S. Per cent.	P. Per cent.	Mn.	C. Per cent.
I	0.031	0.292	Trace	0.06
II	0.032	0.293	Trace	0.06

This steel does weld but breaks on bending, for which reason its manufacture was abandoned.

If the necessary strengths of shipping cylinders for the various gases are figured from the values given in Table II, it will be found that carbonic acid, nitrous oxide and oxygen (under 1,500 pounds pressure) require cylinders made of steel of high tensile strength, while cylinders for ammonia and compressed air (under 600 pounds pressure) for railroad cars and for many other gases, can be made from steel of less strength.

Bearing in mind that steel of high tensile strength cannot be welded, while steel of less strength has welding qualities, the manufacture of steel cylinders in this country is carried out in two different ways.

Cylinders made from high-grade steel are made by the seamless method. This class of cylinders is represented by carbonic acid cylinders and cylinders for nitrous oxide gas and oxygen.

Fig. 5.

The second type of shipping cylinders

is made from steel of less strength which has welding qualities, and this type of cylinders is used for liquefied ammonia gas and compressed air under less than 600 pounds pressure.

Their mode of manufacture is as follows: A sheet of steel, about 25 feet long and of a width equal to about $3^{1}/_{4}$ times the diameter of the tube which is to be made, is heated in a furnace (Fig. 2) to welding heat, whereupon it is drawn over a core through a round die, forming a tube of such diameter that the edges of the sheet overlap one another and by pulling the sheet with great force over the core and through the die, the weld is pressed together so that it does not exceed in thickness the original plate. Cutting off the crop ends from the tube, a length of about 22 feet is obtained which is put into the testing bench, in which both ends of the tube are closed by suitable pistons. This done, water under about 600 pounds pressure is applied to the interior of the tube, whereby leaks may be detected and whereby the entire tube is rounded out into a uniform shape. If the tube has proved sound, it is cut in suitable lengths, which serve for the manufacture of shipping cylinders.

Circular plates are cut for the heads and while hot are dished and flanged in a suitable press.

A boss is welded to the center of one head for each cylinder, to give sufficient metal for the hole receiving the valve and the heads are pressed into the ends of the cylinders, heated to a welding point, pressed together and flared between conical rollers, as shown in Fig. 3, whereupon the cylinders are ready for testing.

The testing includes an inspection for visible defects, the ascertaining of their length, diameter and weight, a test of the material for ductility and strength, and the test of the finished cylinder by pressure test.

For the test of ductility of the material, the crop ends may be used which constitute the waste in cutting tubes for cylinders to length. The test for ductility is made by bending test strips to four times the thickness of the material, whereupon no cracks must be visible on the bends (Fig. 4).

The test for strength of the material may be made by cutting test strips from the crop ends, finishing them as indicated in Fig. 5 and pulling them in a testing machine to destruction. If waste material has not been saved in cutting pipes, a number of cylinders, say one out of 200, are cut up for the purpose of obtaining test pieces. Cylinders, the measures and weights of which are beyond the limits or the material of which is deficient or which, upon inspection, show deformities or defects, are rejected without further test.

The finished cylinders are subjected to the following pressure tests:

Preliminary Test.—A hydrostatic pressure of 1,000 pounds to the square inch is put on to round up the cylinders and to detect leaks. If, upon inspection after this test, the cylinders do not show any leak, local weakness or any visible defect, they are subjected to the

Water-jacket Test, to ascertain their elasticity and permanent expansion. The test is made in the apparatus illustrated in Fig. 6.

A steel cylinder, B, closed at one end and of sufficient size to receive the cylinder A, which is to be tested and having a cover of a design similar

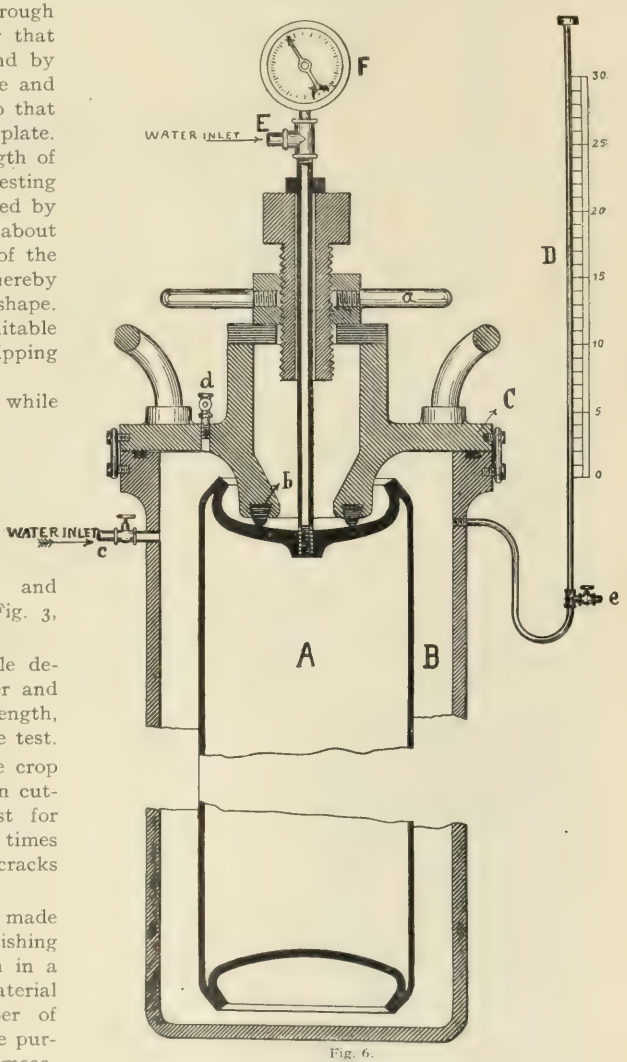


Fig. 6.

to C, in Fig. 6, is set in an upright position, and is connected with a gauge tube, D, which in turn is provided with a scale divided in inches and tenths.

The apparatus is operated as follows:

Vessel B (called the jacket) is filled with water and cylinder A, also filled with water, is lowered into jacket B, care being taken that all the air is removed by means of a bent pipe from the cavity in the lower head of the cylinder. Cover C is put on, fastened with suitable clamps, and by screw-

ing up the hand wheel *a*, the joint is made watertight between the rubber gasket *b* and the head of the cylinder. By opening valve *c*, water is admitted to B which drives out all the air from the apparatus through the escape valve *d*. After closing *d* the water rises to the top of the gauge glass D, and sufficient water is allowed to run from the tube to remove all the air from the apparatus, whereupon valve *c* is closed. By manipulating valve *e*, the water column in D is adjusted to zero on the scale, and the apparatus is ready for the test.

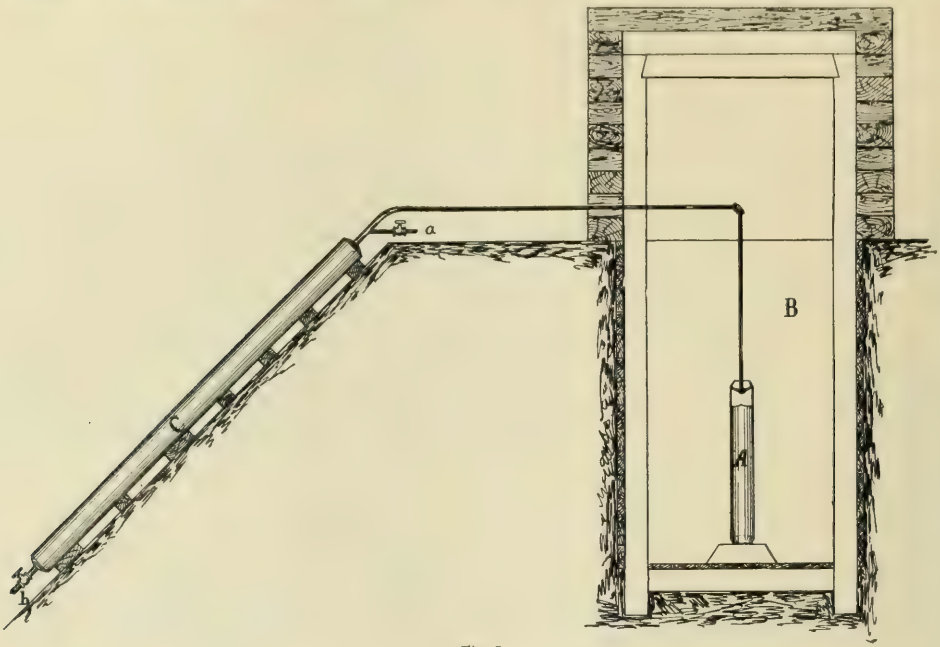


Fig. 7.

Fig. 8

Water under high pressure is now admitted through tube E, to the interior of cylinder A, the pressure being observed on the gauge F. With increasing pressure, cylinder A expands and drives an amount of water equal to the cubic expansion of the cylinder into the gauge glass D, where its volume is read off by the scale. In a specific instance, the water column in tube D rose 11.1 inches and this value represented the total cubical expansion of the cylinder under the prevailing pressure, which, in this instance, was 1,000 pounds to the square inch. Upon relieving the pressure, cylinder A contracted to near its former volume, the water column in D at the same time receding towards the zero mark. In the instance referred to, the water receded to 0.35 inch on the scale, which represented the permanent expansion of the cylinder caused by the application of 1,000 pounds pressure, and the quotient $\frac{0.35 \times 100}{11.1} = 3.1\%$ indicated the permanent set, expressed in per cent. of the total expansion.

If the permanent set is less than 10% of the total expansion, the cylinder is considered safe for use and is accepted.

These are the tests prescribed by the regulations.

For the purpose of investigating how cylinders behave under other conditions, some additional experiments were made, which may be briefly mentioned.

TEST OF A CYLINDER, 10 INCHES BY 7 FEET, 167 POUNDS, 0.19-INCH WALLS. 7.2 PARTS ON THE SCALE = 100 CC.

Pressure. Pounds.	Exp. on scale.	Set on scale.	Set per cent. of exp.	
400	4.4	0.1	2.3	
500	5.4	0.2	3.7	
600	6.6	0.2	3.0	
700	7.7	0.25	3.2	
800	8.9	0.25	2.8	
900	9.9	0.25	2.5	
1000	11.1	0.35	3.1	
1050	11.7	0.5	4.3	
1100	12.5	0.8	6.4	
1150	13.5	2.4	17.8	yield point

1. Subjecting a cylinder to water jacket test and ascertaining expansion and set at various pressures: The experiment was made in apparatus Fig. 6 and the results are entered in the preceding table.

2. Subjecting a cylinder to hydropneumatic pressure to destruction, done for the purpose of ascertaining whether cylinders made from certain materials will break up into flying fragments if they are exploded by gas pressure:

The arrangement of the experiment was as shown in Fig. 7.

Cylinder A was set in pit B, which was dug into the ground and protected by heavy timbers.

On a near-by river bank, cylinder C (having five times the size of A), of heavy material and previously tested by internal hydrostatic pressure at 3,000 pounds to the square inch, was set at an angle of 45°, the top of this cylinder being connected with cylinder A by a $^1/_2$-inch extra strong pipe. Both cylinders were filled with air at 100 pounds pressure by valve *a*, whereupon valve *a* was closed. Subsequently water was admitted under high pressure by valve *b* into cylinder C, increasing gradually the air pressure and driving the air from cylinder C into cylinder A until explosion occurred.

An exploded cylinder is represented by Fig. 8. It was burst open, not sending out any fragments of metal in its destruction.

3. Subjecting a cylinder to drop test for the purpose of ascertaining whether cylinders of certain materials charged with compressed gas will break if they are dropped in a loaded condition from a platform, wagon or car, landing crosswise on another cylinder of the same description, lying on the ground:

The experiment was arranged as sketched in Fig. 9. Cylinder A was put in a horizontal position

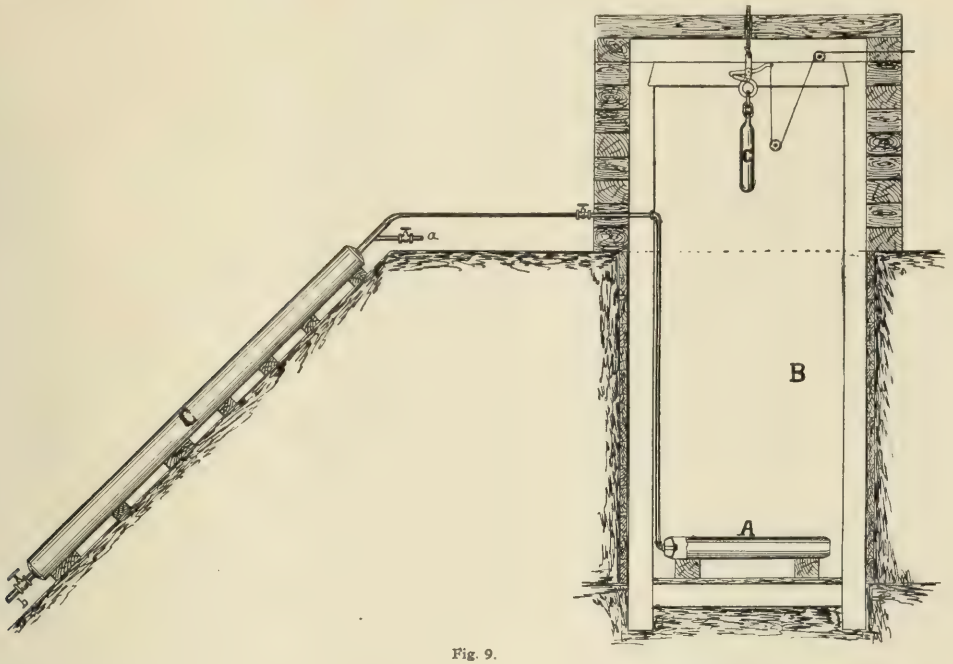


Fig. 9.

into pit B, connected up to cylinder C and filled with air of the desired pressure.

A drop weight, G, having the weight of a cylinder filled with ammonia, was suspended over the center of the cylinder and was dropped by releasing the lock. Two pictures (Fig. 10) show the indentations made by the weight. There being no fracture, the conclusion was drawn that the cylinders could have dropped from an equivalent height, without causing a serious accident by explosion.

Fig. 10

PRESSURE GAUGES USED FOR THE TESTS AND EXPERIMENTS.

Attention is called to the unreliability of commercial pressure gauges under high pressures. Variations as high as 10% were repeatedly found, and it is necessary to make frequent comparisons with dead-weight testing apparatus to ascertain the correctness of the instruments.

The apparatus used for controlling the gauges in the described experiments was of the design as offered by the American Steam Gauge and Valve Manufacturing Company, of Boston, Mass., the accuracy of which was controlled by the United States Bureau of Standards and found to be correct within a fraction of one per cent.

(*Continued in the next number.*)

THE MANUFACTURE AND TESTING OF CARBONIC ACID CYLINDERS.[1]

By JOHN C. MINOR, JR.

Received Dec. 26, 1911.

The manufacture of liquefied carbonic acid was begun in this country about thirty years ago and has expanded to an industry of considerable magnitude. While its uses are of a varied nature, it is as the essential ingredient of carbonated beverages that carbonic acid has become an important article of commerce.

Until very recently there were no traffic regulations in this country covering the shipment of compressed gases, nor was there—unless perhaps in isolated cases—any effort on the part of manufacturers of such gases to procure gas cylinders of any distinctive type or particular quality. It was considered sufficient that the cylinders had—by a custom inherited from Germany—passed a hydrostatic test of 3700 pounds per square inch.

In 1896 a British Parliamentary Committee made a lengthy investigation of questions relative to the safe transportation of compressed gases, and certain regulations were recommended in its report but did not become official. They mainly summarized what was in most respects the prevailing British practice and when later they were largely embodied in the British railroad transportation requirements but little difficulty was found in complying with them.

In Germany there were at that time Governmental regulations regarding the filling and testing of such cylinders, but only within comparatively recent years were these extended to cover the manufacture of the cylinders.

In this country the transportation of all dangerous or inflammable articles is now carried on under the regulations of the Bureau of Explosives of the American Railway Association as approved by the Interstate Commerce Commission. The Bureau, through its chief, Col. B. W. Dunn, first took up the matter of compressed and liquefied gases early in 1909.

There had already been some careful and extensive work done on this subject by Prof. R. T. Stewart, of the University of Pittsburg. In his paper, "The Physical Properties of Carbonic Acid and the Conditions of its Economic Storage for Transportation," read in December, 1908, before the American Society of Mechanical Engineers—and from which the writer has freely drawn—are to be found in condensed and usable form valuable data relative to the physical properties of carbonic acid.

The National Tube Company of Pittsburgh had also instituted a preliminary investigation of the subject and when, at the suggestion of the Bureau of Explosives, the manufacturers of liquefied gases determined upon an investigation of the cylinder question, every facility was offered them by that company to make it complete and to it is due the credit of much of the cylinder data here presented.

Before considering the cylinders themselves several facts regarding carbonic acid may be noted. This product may appear in transit either in liquid form, or as a vapor, or in both conditions, together. Its critical temperature is 88.4° F., above which it cannot exist in liquid form. At any temperature below this, all of the cylinder may be filled with the liquid gas or a part of it may be filled with the liquid and the remainder with the saturated vapor. Just as long as there is saturated vapor present, the pressure will be constant for a fixed temperature without reference to the proportion of liquid present, but when the cylinder becomes entirely filled with the liquid the pressure will no longer be constant for a fixed temperature

It is obvious that the condition, whether gaseous, liquid, or both, that obtains below the critical temperature within the cylinder and the pressure thereby exerted on its walls is dependent on the relation existing between the total capacity of the cylinder and the amount of carbonic acid which it contains. This relation is expressed by Professor Stewart in his table appended hereto, as the density and represents the proportion of filling in pounds of carbonic acid per pound of water capacity, being for each condition tabulated, the combined densities of the liquid and its saturated vapor and being equal in each case to their combined weights divided by the weight of their combined volumes of water at its maximum density; that is, a density of 0.75 would mean that a cylinder which could hold 100 lbs. of water had 75 lbs. of carbonic acid in it, or a cylinder with a water capacity of 80 lbs. contained 60 lbs. of carbonic acid.

Reference to this table of Professor Stewart will show for any given proportion of filling or density, the pressure exerted by carbonic acid within the cylinder for any given temperature and which it must under all conditions safely resist. These pressures are increased by about 60 lbs. per sq. in. for each per cent. of air present. Manifestly, strength to resist pressure is only one feature of a properly designed cylinder and ability to withstand rough handling in transportation and to resist fragmentation on fracture are other important elements in the problem of producing a safe cylinder.

Carbonic acid gas cylinders are made in this country by three different processes.

In the plate process, a circular plate, of a thickness and diameter corresponding to the size of cylinder to be manufactured, is heated and punched into a half spherical cup (Fig. 1). This cup is then pushed

[1] Paper presented at Annual Meeting, American Institute of Chemical Engineers, Washington, December, 1911.

TABLE I.

PRESSURE EXERTED BY CARBONIC ACID ON WALLS OF CONTAINING VESSEL IN POUNDS PER SQ. IN.

FROM PROF. STEWARTS' PAPER.

DENSITY Water at 39.2°F.=1	Temperature in Degrees Fahrenheit									Temperature in Degrees Fahrenheit									
	32°	40°	50°	60°	70°	80°	90°	100°	110°	120°	130°	140°	150°	160°	170°	180°	190°	200°	212°
50	504	565	650	744	849	965	1095	1245	1395	1550	1710	1870	2030	2185	2345	2505	2665	2825	3020
51	504	565	650	744	849	965	1100	1250	1405	1560	1730	1895	2055	2220	2385	2550	2715	2880	3080
52	504	565	650	744	849	965	1100	1255	1415	1580	1750	1915	2085	2255	2425	2595	2765	2930	3140
53	504	565	650	744	849	965	1100	1260	1425	1600	1770	1940	2115	2290	2465	2640	2815	2990	3205
54	504	565	650	744	849	965	1105	1265	1440	1615	1790	1970	2145	2325	2505	2685	2870	3050	3270
55	504	565	650	744	849	965	1105	1270	1450	1630	1810	1995	2180	2365	2550	2735	2925	3110	3340
56	504	565	650	744	849	965	1105	1280	1465	1650	1835	2025	2215	2405	2600	2790	2980	3175	3410
57	504	565	650	744	849	965	1110	1290	1475	1670	1860	2055	2255	2450	2650	2845	3045	3245	3490
58	504	565	650	744	849	965	1110	1300	1490	1690	1885	2090	2295	2495	2705	2905	3115	3320	3570
59	504	565	650	744	849	965	1115	1310	1505	1710	1915	2125	2335	2545	2760	2970	3185	3395	3655
60	504	565	650	744	849	965	1115	1320	1520	1735	1945	2160	2380	2595	2815	3035	3255	3475	3740
61	504	565	650	744	849	965	1120	1330	1540	1760	1975	2200	2425	2645	2875	3100	3330	3555	3835
62	504	565	650	744	849	965	1130	1340	1560	1785	2010	2240	2475	2700	2940	3170	3405	3640	3925
63	504	565	650	744	849	965	1140	1355	1580	1815	2044	2285	2525	2760	3005	3240	3485	3725	4020
64	504	565	650	744	849	965	1150	1375	1605	1845	2080	2330	2575	2820	3070	3315	3570	3825	4120
66	504	565	650	744	849	985	1160	1395	1630	1875	2120	2370	2630	2885	3140	3395	3655	3910	4220
66	504	565	650	744	849	965	1175	1416	1660	1910	2165	2430	2690	2955	3215	3480	3750	4010	4335
67	504	565	650	744	849	965 B	1190	1440	1690	1960	2220	2495	2755	3035	3300	3570	3850	4120	4455
68	504	565	650	744	849	975	1205	1465	1725	1995	2265	2544	2825	3105	3390	3670	3955	4235	4580
69	504	565	650	744	849	990	1230	1495	1765	2040	2325	2615	2900	3190	3485	3775	4070	4355	4710
70	504	565	651	744	849	1005	1255	1530	1810	2095	2385	2685	2985	3280	3580	3885	4190	4485	4850
71	504	563	650	744	849	1020	1285	1570	1855	2150	2455	2760	3070	3375	3690	4000	4315	4620	5000
72	504	565	650	744	849	1050	1320	1610	1910	2215	2530	2845	3165	3480	3800	4125	4450	4765	
73	504	565	650	744	849	1080	1360	1660	1970	2290	2610	2940	3265	3595	3925	4260	4590	4910	
74	504	565	650	744	849	1110	1405	1720	2035	2365	2700	3040	3375	3745	4055	4400	4740		
75	504	565	650	744	849	1140	1460	1785	2110	2450	2790	3145	3495	3845	4195	4545	4895		
76	504	565	650	744	870	1190	1515	1850	2190	2535	2890	3235	3620	3980	4340	4700			
77	504	565	651	744	910	1240	1595	1925	2275	2630	3000	3340	3755	4120	4495	4885			
78	504	565	650	744	955	1295	1665	2005	2370	2740	3120	3570	3895	4275	4645				
79	504	565	650	744	1005	1355	1715	2090	2470	2850	3245	3650	4050	4440	4840				
80	504	563	650	744	1060	1425	1795	2185	2584	2935	3385	3800	4210	4645					
81	504	563	650	750	1120	1500	1885	2290	2695	3110	3530	3960	4390	4800					
82	504	563	650	800	1190	1585	1985	2405	2825	3235	3685	4130	4575	5000					
83	504	563	650	860	1260	1675	2095	2530	2965	3410	3855	4315	4775						
84	504	563	650	935	1340	1780	2215	2665	3115	3575	4040	4510	4985						
85	504	563	630	1020	1440	1895	2345	2815	3280	3760	4240	4720							
86	504	563	685	1110	1550	2020	2490	2980	3461	3960	4430	4950							
87	504	563	765	1210	1665	2155	2650	3160	3665	4175	4680								
88	504	564	855	1320	1800	2310	2825	3360	3880	4410	4935								
89	504	565	960	1440	1950	2480	3020	3585	4150	4695									
90	504	655	1080	1585	2120	2675	3235	3800	4385	4971									
91	A 504	760	1215	1755	2305	2880	3470	4050	4625										
92	530	880	1360	1925	2525	3150	3720	4320	4910										
93	620	1005	1525	2120	2740	3375	3995	4610											
94	725	1145	1715	2340	2990	3645	4280	4920											
95	855	1320	1935	2590	3305	3930	4595												
96	1010	1515	2175	2880	3645	4240	4910												
97	1200	1740	2490	3150	3850	4565													
98	1430	2005	2745	3480	4195	4915													
99	1700	2305	3065	3825	4555														
100	2010	2635	3415	4200	4940														

through a series of round dies over an inside mandrel governing the inside diameter (Fig. 2).

In this manner, this cup is elongated and reduced in diameter and thickness of wall until the proper dimensions are obtained. The bottom of this cup

FIG. 1.—CUPPED PLATES.

has the thickness of the original plate, with a slight reduction caused by the several heats through which it has passed, and in the last elongating operation it may be dished or flattened to enable the cylinder to stand upright. The elongated cup is now cut to length and the open end swaged between hammer dies into the shape of a bottle-neck.

After this operation the cylinder is annealed and heat treated as the case may be, and then finished up by threading the neck and testing in accordance with specifications.

FIG. 2.—HOT DRAW BENCH.

In the spinning process a hot, finished, seamless tube, with both ends open, is heated at one end and by a process of "spinning" the end of the tube is closed and welded in the center so as to form a homogeneous bottom in the tube.

The spinning process itself is very simple. The spinning machine is a type of lathe with a hollow spindle, so adapted that cylinders or tubes to be spun may be put into it and chucked, with the end which is to be worked extending outside of the chuck. This end having been heated, the tube is put into the lathe which is then rotated at from 1200–1400 revolutions per minute. At that speed, a tool is brought to bear against the rotating end of the tube. This tool, sweeping the end of the tube in a half-circle, forces its sides to meet in the center, where the high heat, caused by the friction of the tool against the tube, produces a perfect weld in the center.

The bottom thus formed is then dished or flattened, or a loose ring may be shrunk around it to enable the cylinder to stand upright. The necked end is produced as already described under the plate process.

In the lap-weld process, now obsolete, a lap-weld tube of the proper dimensions is used and one end is necked down over a plug about 4 in. in diameter by 1 in. thick. This plug is welded into the neck end of the cylinder, thus forming the head. The bottom is formed by welding a half spherical cup into the bottom end, with the concave side of the cup out, thus enabling the cylinder to stand on its bottom. The annealing, testing, etc., as above described, also applies to this cylinder.

In the plate process, cylinders from 3″ diameter up to 20″ diameter are made.

In the spinning process, cylinders from 1″ diameter up to 6″ diameter are made.

In the lap-weld process, cylinders from 3″ diameter up to 8″ diameter have been made.

There are in use in this country for conveying carbonic acid several sizes of cylinders of both the seamless and lap-welded types, of which the larger part are the 5-1/2″ × 51″ and 5-1/2″ × 48″ lap-welded and the 8-1/2″ × 51″ seamless cylinders. The 5-1/2″ cylinders are filled with 20 lbs. of gas giving a filling density of 0.66 for those of 48″ length and of 0.57 for those 51″ long. The 8-1/2″ cylinders are filled with 50 lbs. of gas giving a filling density of 0.57.

The present paper is devoted only to the subject of the seamless cylinders, as the tendency in high-pressure work, *i. e.*, 1,000 lbs. and over, has been to develop that type in preference to the lap-welded cylinder.

In the preparation of regulations to govern the transportation—and later, the manufacture—of cylinders it was necessary to assume a maximum temperature to which cylinders in transit might be exposed. In Germany the revised regulations set this at 104° F. but in this country it was fixed by the Bureau of Explosives at 130° F.

Reference to Professor Stewart's table shows that with the fillings mentioned above and a temperature of 130°, the 5-1/2″ × 48″ cylinder would have a pressure of 2210 lbs. per sq. in., while the pressure in the 5-1/2″ × 51″ and the 8-1/2″ × 51″ cylinders would be 1860 lbs.

The British standard as recommended by the Parliamentary Committee in 1896 is as follows:

Carbon—Not to exceed 0.25 per cent.

Iron—Not to be less than 99.00 per cent.

Elongation—On 8″ bar from finished cylinder not to be less than 15 per cent.

Tensile Strength—Not to be less than 63,000 lbs. nor more than 74,000 lbs.

All cylinders to be annealed before putting in service.

A large number of seamless cylinders of this character, known as the Linde cylinders, and used for compressed oxygen, have been made in this country under a slightly different specification, briefly as follows:

Carbon, not to exceed 0.25 per cent.

Manganese, not to exceed 0.60 per cent.

Phosphorus, not to exceed 0.04 per cent.

Sulphur, not to exceed 0.04 per cent.

Silicon, not to exceed 0.35 per cent.

Elongation, not less than 15 per cent.

Tensile strength, not less than 62,000 nor more than 76,000 lbs.

All cylinders to be annealed, and to pass a hydrostatic sketch test of 3600 lbs. per sq. in.

Representative cylinders to be submitted to a flattening test.

This, of course, is a mild, ductile steel and there had been a somewhat prevalent impression that a cylinder of such metal, if exploded from fire or other causes, would not fragment, but merely open up and thus greatly reduce the chance of personal injury and, indeed, it has been towards obtaining such a cylinder, if possible, that recent efforts have been mainly directed. It was recognized, however, that the large carbonic acid cylinders must carry a load of 50 lbs. of gas; that a maximum temperature of 130° was assumed against 104° on the other side; that our freightage distances and rates were very considerable; and that in view of all this we could not consider a cylinder which like the English or Linde type would weigh, when empty, about 170 lbs.

In view of the absence of data concerning cylinders already in use in this country, samples were selected at random from various parts of the country. The experiments performed consisted of:

1. Tensile tests of material cut in longitudinal direction. Data appended. (See Table II.)

2. Bending tests of samples cut in transverse direction. These were bent until fracture occurred and in all but a few instances the bend was through an arc of 180° about a mandrel whose diameter was less than four times the thickness of the specimen.

3. Transverse tests of whole cylinders (Fig. 3). Several representative cylinders were tested by placing them on two bars of iron, one inch wide and spaced nine inches on centers and applying a center load through a piece of shafting 2-1/2″ in diameter. These tests showed that a very considerable amount of distortion was endured before even the poorest

cracked. The low carbon cylinders did not crack at all.

4. Chemical analyses. Data of these are appended.

5. Hydraulic bursting tests (Fig. 4). Water was forced into the cylinders until rupture occurred. Two small lap-welded cylinders ruptured along the weld, each at a pressure of 4400 lbs. One large seamless cylinder burst at 5600 lbs. The form of fracture seemed characteristic in all, as shown by the photographs.

6. Fire tests. Cylinders were filled with their usual capacity of carbonic acid and placed in the open over a hot fire of oil-soaked wood. It took 8 to 12 minutes' direct exposure to produce rupture.

Cyl. No. 1 (Fig. 5). Large seamless type. Carbon, 0.56 The bottom was blown off, the cylinder split in halves and a piece about 6" × 8" blown off near shoulder.

Cyl. No. 2. Small lap-welded type. Carbon, 0.11. Ruptured along weld without fragmentation.

Cyl. No. 3. Large seamless type. Carbon, 0.63. Bottom blew off but no other fracture.

Cyl. No. 4 (Fig. 6). Large seamless type. Carbon, 0.55. Bottom blew off. Remainder flattened out.

Cyl. No. 5. Large seamless type. Result like No. 4 except two pieces of shoulder flew off.

7. Expansion tests. Three cylinders were subjected to hydraulic pressure in water jacket until sufficient pressure was applied to stress the material to its elastic limit. This was found to be about 4,000 lbs. in each case.

TABLE II.

PHYSICAL AND CHEMICAL TESTS ON CYLINDERS IN SERVICE

	t	d	E L	ULT	% El 2"	% Red Area	C	P	S	Mn	Si
Small Lapwelded Cylinders											
G	300	5.30	38070	59040	20.4	57.9	.12	.097	.063	.701	.018
H	290	5.50	37970	57140	23.0	53.4	.10	.123	.070	.492	.010
I	314	5.50	37970	57980	21.5	57.6	.12	.114	.088	.418	.007
J	300	5.50	39720	56330	21.5	57.7	.10	.123	.096	.420	.019
X	320	5.60	41300	57490	20.2	58.9	.10	.103	.067	.455	.012
Y	278	5.60	38780	61030	23.0	52.6	.11	.110	.076	.455	.005
AA	311	5.56	37670	60100	19.6	58.7	.11	.119	.073	.522	.003
AVERAGE	1718	5.55	38670	57710	21.9	57.0	.11	.111	.076	.495	.012
Large German Seamless											
Q	250	8.18	61890	64340	2.00	42.9	.65	.049	.051	1.11	.180
R	285	8.00	61160	76370	1.01	39.3	.14	.054	.032	1.18	.110
S	240	8.01	70930	76960	1.50	48.6	.33	.061	.044	1.16	.175
T	338	8.44	71090	87700	1.09	41.6	.14	.092	.039	.648	.110
U	333	8.40	69380	98350	1.60	40.5	.19	.101	.068	.971	.248
AVERAGE	1296	8.33	66020	80210	1.99	42.8	.25	.079	.059	1.02	.160
Large American Seamless open hearth											
C	330	8.19	39870	107100	13.5	39.1	.69	.035		.691	
E							.58	.057		.658	
L	250	8.00	66300	111150	11.6	36.9	.50	.046	.033	.845	.163
M	250	8.06	60570	102250	14.0	33.9	.42	.035	.038	.920	.039
N	230	8.06	60820	122130	12.0	27.8	.57	.092	.042	.651	.071
O	240	8.05	74870	116510	10.8	21.9	.60	.028	.089	.709	.134
P	215	8.06	85210	128930	6.3	24.6	.67	.019	.082	.598	.110
V	230	8.1	67590	97210	16.2	30.6	.45	.030	.044	.737	.033
W	242	8.22	69180	113950	11.2	19.6	.47	.039	.030	.794	.017
AVERAGE	2402	8.09	67380	111430	11.9	27.0	.53	.039	.044	.693	.075
Large American Seamless Bessemer											
B	333	8.40	64160	88940	15.2	41.8	.21	.110		.758	
K	250	8.25	71470	90100	13.8	41.4	.15	.107	.056	.725	.180
Z	283	8.40	58710	93350	16.0	39.1	.18	.110	.066	.525	.136
AVERAGE	2217	8.28	64780	90790	15.0	42.4	.17	.109	.061	.613	.158

These tests were made on cylinders which had been in service for from three to seventeen years and were conducted at the laboratories of the Rensselaer Polytechnic Institute at Troy and in the field at Saratoga.

No one of the lap-welded cylinders shows in any feature a marked departure from the general average of the lot except Cyl. G. which has 0.701 manganese against an average of 0.495, a fact which does not appear to be reflected in any physical feature of the cylinder.

The high phosphorus in all of this group averaging 0.111 is a marked characteristic and as a prejudicial hardener opens this type to criticism. Nevertheless, the broken specimens showed a fairly reasonable degree of ductility.

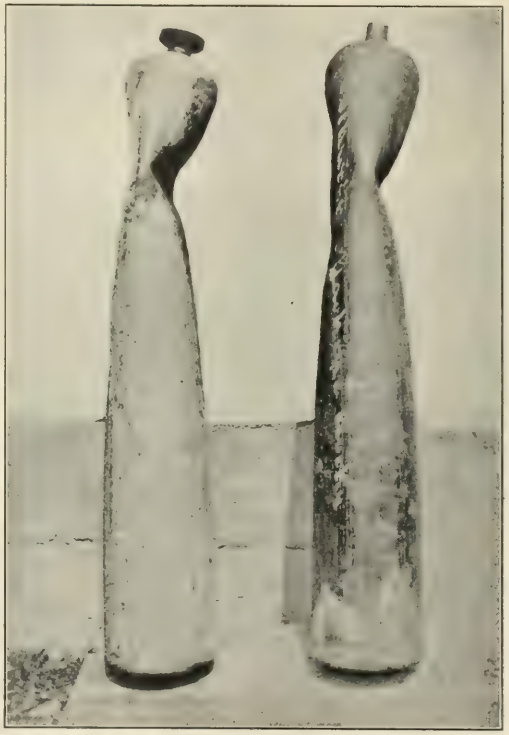


FIG. 3.—TRANSVERSE TESTS.

The German cylinders showed very different steel from that offered in this country for cylinders. They vary from 0.14–0.45 carbon, run high in silicon—from 0.110–0.248—and with one exception are very high in manganese, averaging 1.02. These high manganese cylinders, whether of German or American make, not only show satisfactory ductility but exhibit high values of ultimate reduction of the fractured section.

There was disclosed by these tests an irregularity of chemical contents and corresponding physical results which are not desirable in metal which it is possible to standardize, but it was felt that they

justified the general observation that the cylinders might be considered safe for transportation under such pressures as would in no case produce stresses greater than $^3/_4$ of the elastic limit. They also emphasized the desirability of ascertaining and prescribing the most suitable metal for this work.

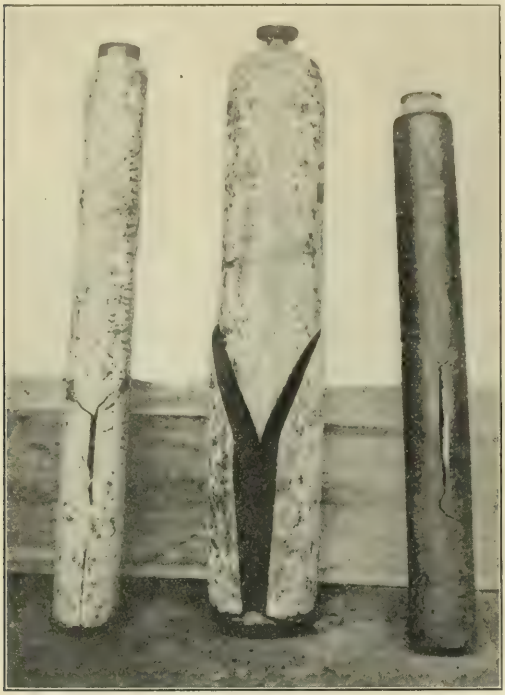


FIG. 4.—HYDRAULIC TESTS.

Work was then directed along this line and the following specifications tentatively adopted. In view of the results subsequently obtained in the various tests briefly outlined below they were later incorporated, through the Bureau of Explosives, in the Regulations of the Interstate Commerce Commission, becoming effective October 1st, 1911.

SPECIFICATIONS FOR SEAMLESS STEEL CARBONIC ACID GAS CYLINDERS AS APPROVED BY THE BUREAU OF EXPLOSIVES, AMERICAN RAILWAY ASSOCIATION.

Cylinders are to be made seamless, of steel of uniform quality, to comply in the present state of the art with the following specifications:

CHEMICAL ANALYSIS.

Carbon is not to exceed	0.55 per cent.
Phosphorus is not to exceed	0.04 per cent.
Sulphur is not to exceed	0.05 per cent.

PHYSICAL TESTS.

Elastic limit is not to be less than 50,000 pounds, nor more than 65,000 pounds per square inch on specimen cut longitudinally from a representative finished cylinder after annealing.

Elongation is not to be less than 10 per cent. on an 8" length of longitudinal test specimen cut from a representative finished cylinder after annealing.

FLATTENING TEST.

For each lot of 200 a representative finished cylinder, after annealing, is to withstand, without cracking, flattening between rounded knife edges to a thickness four times the thickness of the wall of the cylinder. The knife edges are to be of wedge shape, converging at an angle of 60°, the point being rounded off with a radius of one-half inch. If any one cylinder from any lot fails to pass this test, two others from the same lot will be selected, and these must pass it in order to have the lot accepted. If it should appear that failure in the test was due to improper annealing, the manufacturer has the privilege of re-annealing the lot and repeating the test.

One out of each 200 cylinders is to be subjected to the above chemical, physical and flattening tests.

ANNEALING.

All cylinders after finishing are to be uniformly

FIG. 5.—FIRE TEST, CYLINDER NO. 1.

and properly annealed; dirt and scale are to be removed before painting.

HYDROSTATIC TEST.

Every finished and annealed cylinder is to be subjected to hydrostatic test in a water jacket or other

apparatus of approved form, whereby an interior pressure of not less than 3,000 pounds per square inch will be applied. The permanent expansion shall not exceed 5 per cent. of the whole volumetric expansion at this pressure.

THICKNESS.

The wall of cylinders of both 5-1/2" and 8-1/2" outside diameter is not to be less than 0.25" thick and this is to be verified on each cylinder before necking down.

FIG. 6.—FIRE TEST, CYLINDER NO. 4.

WEIGHT.

The standard 8 1/2". × 51" cylinder, without cap, shall weigh not less than 105 pounds, nor more than 115 pounds.

INSPECTION.

The purchaser shall provide for inspection at the mills by a competent and disinterested authority, who shall be provided with a copy of the order containing all information relating thereto other than price. The inspector shall keep complete records of the various melts from which the steel is taken for the manufacture of the cylinders. Chemical analyses of these melts must be supplied to him by the manufacturer, or if desired by the purchaser, he will procure samples from which other chemical analyses may be made. The heat number shall be stamped on these plates at the steel mill by the inspector, and his stamp, when placed on a completely finished cylinder, shall be taken as certifying that such cylinder comes within the above physical and chemical specifications.

The Inspector shall witness the hydrostatic and flattening tests of all cylinders and shall certify to the maker, the purchaser and the Chief Inspector of the Bureau of Explosives, No. 24 Park Place, New York City, the serial numbers of all cylinders which pass them successfully. He shall stamp his initials on such cylinder immediately beneath the serial number, and the initials of the owner shall be stamped on the flange or ring of the cylinder.

The hydrostatic and flattening tests shall be made by the manufacturer, but under the direction and supervision of the inspector, or other representative of the purchaser.

GENERAL CONSTRUCTION.

All plates from which cylinders are made shall be free from seams, cracks, laminations or any defects which may prove injurious to the finished cylinder.

The manufacture of the cylinders must be completed with the best appliances and according to the best modern methods. All finished cylinders must show reasonably smooth and uniform surface finish, inspection of inside surface to be made before necking down; the threading of tap and of flange must be even and without checks, and the cylinders must show no defects of workmanship or material likely to result in any appreciable weakness of the finished cylinder. A close inspection of each completed cylinder shall be made to discover the existence of any defect before acceptance.

Extensive investigations were carried out by the National Tube Co. at McKeesport on cylinders made to these and to other specifications, involving explosion of the cylinders by air pressure, the destructive medium consisting of one part of water to twenty-five parts of air at atmospheric pressure.

Appended (Fig. 7) is a photograph of ten high carbon cylinders thus exploded. These were from

FIG. 7.—AIR TESTS, HIGH CARBON CYLINDERS.

a lot closely approximating the above specifications. They averaged on the unannealed cylinders as follows:

Carbon	0.041
Phosphorus	0.021
Sulphur	0.030
Manganese	0.63
Elastic limit	52,000—55,000 lbs.
Tensile strength	95,000–100,000 lbs.
Elongation	12–14 per cent.
Reduction of area	16–22 per cent.
Weight	95 lbs.

The average yield point of six cylinders before

annealing was 3,400 lbs.—after annealing 2,900 lbs. Four cylinders Nos. 7, 8, 9 and 10 were not annealed. They burst at pressures from 5,500–5,800 lbs. per sq. in. The others were annealed to temperatures varying from 1440°–1800° F. and burst at pressures of from 5,050–5,900 lbs. per sq. in. The fragmentation was poor and showed no appreciable difference between the annealed and the un-annealed cylinder.

In comparison with these results very gratifying results had been obtained at McKeesport on exploding with the same air mixture the low carbon Linde cylinders and especially some cylinders made of chrome vanadium steel. Photographs of both are appended.

The Linde cylinders shown (Fig. 8) averaged as follows:

Silicon	0.192
Sulphur	0.016
Phosphorus	0 015
Manganese	0.50
Carbon	0.23
Elastic limit	36,000 lbs.
Tensile strength	65,000 lbs
Elongation in 8″	27 per cent.
Reduction of area	50 per cent.

All were annealed to 1590° F. Seven of the ten cylinders had no permanent set at 3,300 lbs. pressure. Five yielded at 3,600 lbs. All burst at pressures from 6,550–7,000 lbs. and excepting one, which broke in two pieces, there was no fragmentation, the cylinders merely opening up.

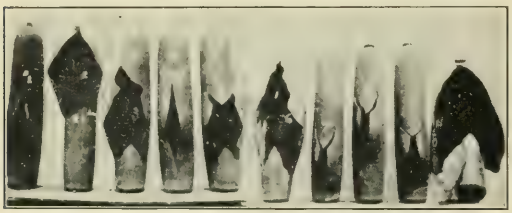


FIG. 8.—AIR TESTS, LINDE CYLINDERS.

The first lot of vanadium cylinders was made up with a $^3/_{16}$″ wall and the weight averaged 77 lbs. against 95 lbs. for the old high carbon cylinders. The cylinders averaged as follows:

Carbon	0.20
Phosphorus	0.049
Manganese	0.60
Silicon	0.031
Chrome	1.05
Vanadium	0.15
Elastic limit	63,500–68,800
Tensile strength	84,000–93,000
Elongation	8.25–16.5 per cent.
Reduction of area	41.8–50.4 per cent.

It should be noted that this test was taken from one of the untreated cylinders. This treatment comprised annealing to 1500°, tempering and re-annealing to about 1000°, and produced quite uniform results. One cylinder which before treatment showed 15 per cent. permanent set at 3,500 lbs., showed after treatment none at 4,000 lbs. and only yielded at 6,250 lbs. The yield points varied from 5,500–6,650 lbs. and the bursting pressures from 6,200–7,100 lbs. per sq. in. One cylinder broke in two pieces but the others stayed whole.

Another lot of vanadium cylinders (Fig. 9) was made exactly like the first except that the wall was made $^1/_4$″ thick, bringing the weight up to 105 lbs. Before treatment all showed less than 5 per cent. permanent set at 3500 lbs. pressure. One cylinder was not treated. It had 8 per cent. permanent set at 4,200 lbs. and burst at 6,350 lbs. pressure. Two were annealed but not tempered. One burst at 5,400 lbs. and the other at 6,000 lbs. Seven were annealed, tempered, and re-annealed, and burst at pressures varying from 6,450–8,500 lbs. The cylinder which had no treatment burst in two pieces but all the others simply opened up a longitudinal split and stayed whole.

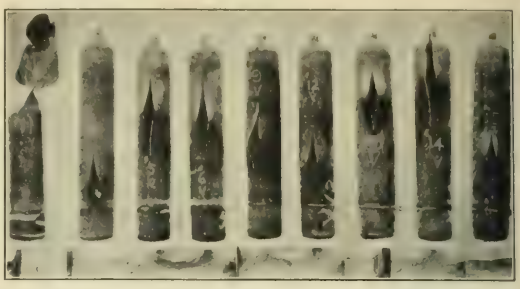


FIG. 9.—AIR TESTS, VANADIUM CYLINDERS.

The photographs show clearly the remarkable results obtained on exploding the vanadium cylinders with air, in comparison with other cylinders burst by the same process. It was, however, difficult to understand why the first lot mentioned, supposed to represent improvement over existing conditions, should have shattered worse than did the type of cylinders in service when the latter were burst with carbonic acid over a fire.

Therefore three cylinders were taken (Fig. 10): One of those made up to the new specifications (N), a Linde low carbon cylinder (L), and a vanadium cylinder (V). Each was filled with carbonic acid

FIG. 10.—FIRE TESTS.

to a density of 0.57 and burst over an open fire at Saratoga. The photograph shows the result. The new high carbon cylinder, as usual with this type, had its bottom blown off, the remainder opening out in one piece. The vanadium cylinder opened up in about the same fashion and at least one good sized piece flew off. The Linde cylinder blew into at least three pieces, only two-thirds of it being found after the explosion.

Another cylinder, No. 1 B, made to the new specifications, was also blown up over fire with very similar results. Its composition was:

Carbon	0.43
Phosphorus	0.010
Manganese	0.625

Another test was of a German cylinder, No. 1 A, about four years old, which on explosion broke in two pieces. Its composition was:

Carbon	0.43
Phosphorus	0.044
Sulphur	0.046
Manganese	1.11
Silicon	0.204

It will be observed that these fire tests gave results differing considerably from those obtained at McKeesport with the mixture of air and water and they were therefore continued at McKeesport, being preceded by several air tests.

Two cylinders made to the new specifications were exploded with air. One burst at 5,500, the other at 5,900 lbs. pressure—no pieces flying and in each case showing two vertical cracks joined by a longitudinal one. A light weight vanadium cylinder opened up one short crack at 5,300 lbs., and a Linde cylinder, at 7,100 lbs., opened up a longitudinal crack extending at each end in two oblique directions.

The fire tests at McKeesport were made on cylinders R-4, R-6, R-7 and R-8 of the following composition:

Carbon	0.41
Sulphur	0.030
Phosphorus	0.021
Manganese	0.63

Also on Cylinder H, of the composition:

Carbon	0.59
Sulphur	0.031
Phosphorus	0.020
Manganese	0.69

These were all unannealed. Both types on explosion gave about the same result and, for some reason, appreciably different from that obtained at Saratoga in the fire tests heretofore mentioned. The method of applying the heat at McKeesport was such as to require from one-half hour to an hour to produce explosion, whereas at Saratoga it took about ten minutes.

It had, therefore, been demonstrated by these tests, that no type of seamless cylinder yet available could withstand explosion from heat without fragmentation and that the new specifications would furnish a satisfactory cylinder, and they were therefore formally adopted.

In comparison with the varied results obtained in this investigation, it is of interest to note some of those in the tests of the first two lots made to order after the new specifications became official.

Test cylinders (Fig. 11) from order No. 6,210 averaged:

Carbon	0.45
Phosphorus	0.019
Sulphur	0.034
Elastic limit	54,700
Tensile strength	84,600
Elongation	18 per cent.
Weight	112 lbs.

Cylinder B-3 burst under air at 5,600 lbs. and B-4 at 5,000 lbs. Neither had any permanent set at 3,000 lbs.

FIG. 11.—TESTS ON ORDER NO. 6210.

Test cylinders (Fig. 12) from order No. 5,623 averaged:

Carbon	0.45
Phosphorus	0.017
Sulphur	0.034
Elastic limit	55,700
Tensile strength	90,900
Elongation	15.5 per cent

Cylinder B_1 burst under air at 5,200 lbs., B_2 at 5,650 lbs. and B_3 at 5,600 lbs.

It will therefore be seen that on the whole there is reason for the belief that the new specifications mark a decided advance in the making of carbonic acid cylinders.

Both the new specifications and the Interstate Commerce regulations require a hydrostatic stretch

FIG. 12.—TESTS ON ORDER NO. 5623.

test and the latter provide for its repetition every five years at a pressure not less than one and a quarter times the interior pressure that would result from heating the cylinder in its maximum charged condition to a temperature of 130°. A cylinder must be condemned if the permanent expansion exceeds 5 per cent. of the total expansion.

Two methods may be used to conduct such tests with the required accuracy. In the water jacket method the cylinder to be tested is filled with water

and submerged in a large tube or jacket through whose removable, but water-tight, cover passes the pipe connecting the cylinder with the high-pressure pump. The jacket is provided with a graduated glass tube like a gauge glass, to act as an expansion indicator, and is completely filled with water, after which the level in the glass tube is noted. The test pressure is then applied to the cylinder and the levels noted during and after the application, the water in the jacket being forced into the glass tube as the cylinder expands and receding to its former level after removal of pressure if there has been no permanent expansion. The other method (Fig. 13) involves the use of the Sturke-Watson-Stillman testing machine and dispenses with a water-jacket. This machine consists essentially of a screw displacement piston which forces enough water into an already filled cylinder to produce the desired pressure.

Attached to the pump cylinder are two graduated glass tubes, one serving as the expansion indicator, the other, back of the stuffing box, as the leakage indicator. The exact delivery of the pump per turn of screw is known and provision made for registering each turn or fraction thereof.

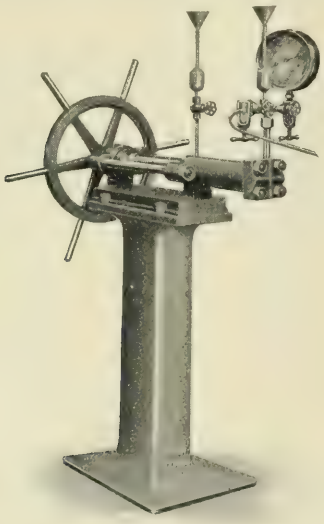


FIG. 13.

Assuming the cylinder under test to be full of water and all connections between it and the pump free of air, a reading is made of both indicators and the position of the piston accurately noted on the graduated scale provided for that purpose. The expansion indicator is then closed off with a valve, and the hand wheel turned until the desired pressure is attained after which the piston is carefully returned to exactly its original position and the valve to the expansion indicator re-opened. It is plain that if the cylinder suffered any permanent expansion its water-containing capacity must have been increased. The extent of this is measured by noting the new level—if such there is—in the expansion indicator after opening the valve.

In calculating the total expansion, proper allowance must be made for the compressibility of the water in both pump and cylinder and for the volume displaced as indicated on the graduated scale.

This method requires more care than the water-jacket method, but when properly conducted is more expeditious and avoids not only the discomforts attendant upon the raising of cylinders from immersion in water but also the necessity of any lifting whatsoever.

LABORATORY GENERAL CARBONIC CO.,
NEW YORK CITY.

THE COMPOSITION OF SOME MINE GASES, AND A DESCRIPTION OF A SIMPLE METHANE APPARATUS.[1]

By G. A. BURRELL.

Received Dec. 15, 1911.

The Bureau of Mines has, in the study it has been making of mine gases, examined samples taken under different conditions, some of which are here presented, also some analytical results obtained in related experimental work.

NO. 1 SERIES.

No. 1 Sample: Incomplete combustion of methane. Original mixture contained 10.03% CH_4.

Products found after explosion	10.16% CO_2
	2.13% CO
	1.39% H_2
	86.32% N_2
	0.00% O_2
	0.00% C_2H_4
	0.00% CH_4

No. 2 Sample: Incomplete combustion of methane. Original mixture contained 10.94% CH_4.

Products found after explosion	8.35% CO_2
	4.47% CO
	3.66% H_2
	83.52% N_2
	0.00% O_2
	0.00% C_2H_4
	0.00% CH_4

In these experiments pure methane was prepared and mixed with air in such proportion that not enough of the latter was present for the complete combustion of the methane. The mixtures were then exploded and the products of combustion examined. The most explosive proportion of methane and air contains 9.47 per cent. of methane. When the latter is increased above this figure certain products are formed about which there has been some disagreement. Some investigators have gone on record as saying that no carbon monoxide is formed. According to these experiments the carbon monoxide and hydrogen increase, and the carbon dioxide decreases as the methane content of the original mixture is raised. Olefine hydrocarbons, acetylene, or unburned methane were not found in the products of combustion. The carbon monoxide and carbon dioxide formed satisfies the carbon originally present

[1] Paper read at the December Meeting of the Coal Mining Institute of America by permission of the Director of the U. S. Bureau of Mines.

in the methane. These figures represent the proportions of gases present in the explosion pipette after the combustion. A contraction in volume of course, took place, consequently the proportions are larger than would be found after a mine explosion where mine air from other parts of the mine would rush in to equalize the pressure. To the carbon monoxide formed in this manner is due some of the carbon monoxide found in the after-damp following mine explosions. Not entirely, however, and in many cases the smaller proportions are formed in this manner, because the incandescent carbon of heated coal dust appears to be mainly responsible for the production of carbon monoxide found after dust explosions.

No. 2 Series.

Crevice samples obtained after explosives had been fired in coal mines.

No. 1 Sample.

	Per cent.
CO_2	16.8
O_2	4.3
CO	22.8
CH_4	17.3
H_2	8.9
N_2	29.9

No. 2 Sample.

	Per cent.
CO_2	9.1
O_2	7.5
CO	3.2
CH_4	14.1
H_2	4.1
N_2	62.0

No. 2 series of samples show the gases formed by firing blasting explosives in coal mines. Both black powder and permissible explosives produce noxious gases. These samples were taken from the crevices produced by the breaking down of the coal. The explosive and noxious character of the gases will be observed, and accounts for the fact that the miner is sometimes burned when he innocently puts his lamp to the coal to examine the effects of his blast.

No. 3 Series.

No. 1 Sample.—Crevice sample taken immediately after shot A had been fired.

	Per cent.
CO_2	1.40
O_2	19.31
CO	1.45
CH_4	1.40
H_2	0.74
N_2	75.70

No 2 Sample.—Sample taken 4 minutes after shot A had been fired.

	Per cent.
CO_2	0.56
O_2	20.22
CO	0.16
CH_4	0.71
H_2	0.06
N_2	78.29

No 3 Sample.—Crevice sample taken immediately after shot B had been fired.

	Per cent.
CO_2	2.50
O_2	16.91
CO	1.21
CH_4	4.88
H_2	1.06
N_2	73.44

No. 4 Sample.—Sample taken 4 minutes after shot B had been fired.

	Per cent.
CO_2	0.30
O_2	20.61
CO	0.02
CH_4	0.25
H_2	0.01
N_2	78.81

No. 3 series of samples represent further gases obtained after explosives had been fired to break down coal. The crevice samples were obtained by proceeding immediately to the face after the shot had been fired and collecting the samples as the gas exuded from the coal crevices. In each case a wait of 4 minutes was made and then the sampler proceeded to the face to collect another sample at about the place the miner would stand to attend to his shot. In one case 0.16 per cent. of carbon monoxide was found a harmful quantity. These explosives were fired under conditions which do not represent best practice. Other experiments are being carried on by the Bureau to obtain further data on this subject, so as to determine the causes which lead to the production of harmful quantities of noxious gases.

Work thus far accomplished shows that it is bad practice to proceed immediately to the face after a shot has been fired. Even those powders which contain within themselves sufficient oxygen for the complete combustion of the carbonaceous matter present in the explosive produced, when fired in coal mines, some carbon monoxide, due again to reaction with the carbon of the coal dust. Some explosives, however, are themselves very deficient in oxygen.

No. 4 Series.

Combustion of gases from an enclosed area in an anthracite mine.

Sample No.	Date.	Per cent. CO_2.	O_2.	CO.	CH_4.	H_2.
1	Oct. 31	2.2	15.0	0.0	14.0	68.8
2	Nov. 1	2.3	14.6	0.0	18.1	65.0
3	Nov. 2	2.6	6.2	0.0	24.2	67.0
4	Nov. 2	2.9	5.7	0.0	29.3	62.1
5	Nov. 3	2.8	4.1	0.0	34.9	58.2
6	Nov. 6	2.6	3.0	0.0	53.0	41.4

These gases, series No. 4, show the composition of the atmosphere in an enclosed section of an anthracite mine. This section of the mine was sealed off because of a fire which existed in an adjoining section. The fire did not affect the particular area from which these samples were obtained because of a heavy intervening roof fall, consequently the gases represent those trapped and given off normally in a stagnant section, except that a stopping was leaking and some air was finding its way into the interior from the ventilating current. The stopping was tightened and the rapid absorption of oxygen by the coal is shown by the third analyses. Four days later the oxygen had dropped to 3 per cent. Even so, some air was finding access. The rapid accumulation of methane is also shown, 53 per cent. on the sixth day.

No. 5 Series.

Composition of gases from an enclosed area in a bituminous mine.

Sample No.	Per cent. CO_2.	O_2.	CO.	CH_4.	N_2.
1	1.50	0.30	0.00	5.29	92.91
2	1.20	0.30	0.00	5.37	93.13

Series 5 shows the composition of gases from an enclosed area in a bituminous mine. A mine fire had once existed in the area and these samples were collected by means of breathing helmets 9 months after the fire had originated and prior to the reopening of the mine. The oxygen had almost entirely disappeared. The mine is classed as non-gaseous. An accumulation equal to over 5 per cent. methane had taken place.

No. 6 Series.

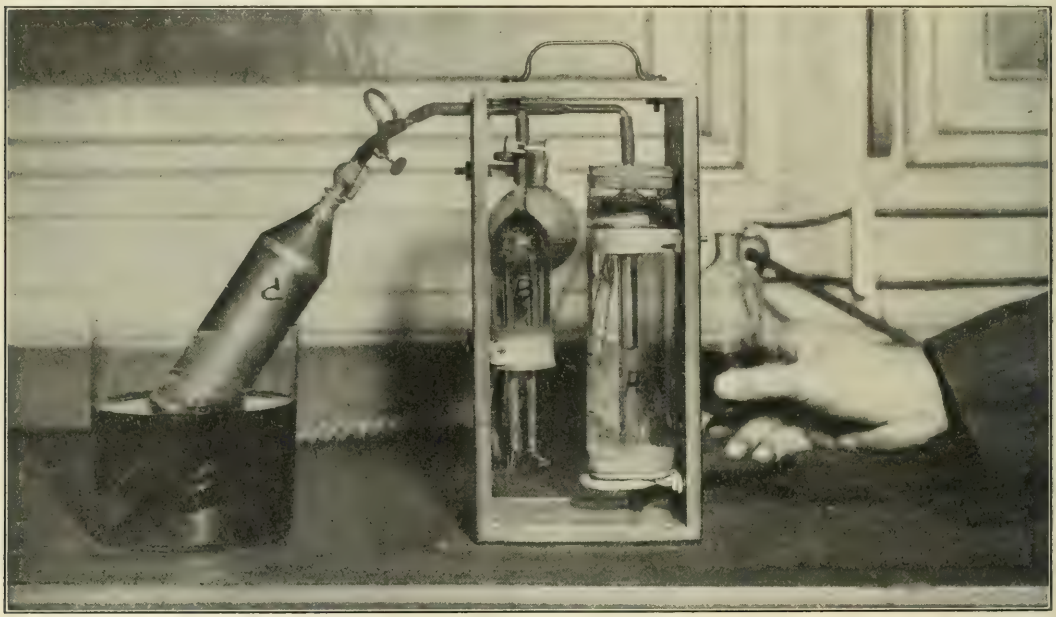
Sample No.	CO_2.	O_2.	CO.	H_2.	CH_4.	N_2.
	Per cent.					
1	8.07	1.69	1.58	1.37	3.39	83.90
2	9.14	1.83	1.32	1.03	3.60	83.08
3	2.93	10.34	0.56	0.13	0.82	85.22

Samples Nos. 1 and 2 in series No. 6 were obtained directly from a fire area, 4 and 7 hours respectively after the mine had been sealed off. The fire occurred just inside the pit mouth of a drift bituminous mine. Samples were obtained by boring holes through the thin roof covering. These analyses with others showed that air was not inleaking to an appreciable extent and the existence of an atmosphere that could not further the progress of the fire. No. 3 analysis of this series represents the atmosphere in the same mine about 1400 feet away from the seat of the fire. An entrance was made through another entry in the mine with oxygen helmets and samples of gas were obtained. The party could not proceed farther because of a heavy fall of smoke. It was impossible to better shut off the air because of various small openings in the outcrop. The oxygen content in sample No. 3 of this series was viewed with some uneasiness, but because of the stagnation of the air and accumulation of black damp it was believed that appreciable diffusion of fresh air into the burning area could not take place. Such proved to be the case.

No. 7 Series.
Mine Fire Gases.

Sample No.	Date.	Time.	CO_2.	O_2.	CO.	CH_4.
			Per cent.			
1	Oct. 27	12.00 P.M.	3.5	8.3	1.3	11.5
2	" 27	12.00 P.M.	3.8	9.6	0.7	13.1
3	" 28	9.45 A.M.	3.4	10.9	0.6	10.8
4	" 28	4.00 P.M.	3.4	11.3	0.6	10.3
5	" 28	4.30 P.M.	3.0	12.6	0.4	9.6
6	" 29	11.00 A.M.	3.3	14 1	0.6	9.0
7	" 29	3.30 P.M.	4.0	13.6	0.8	12.0
8	" 30	10.30 A.M.	4.8	10.1	1.2	14.1
9	" 30	5.00 P.M.	4.0	12.2	1.0	12.2
10	" 31	6.30 A.M.	12.2	6.6	0.4	6.6

Series No. 7 shows the composition of the atmosphere in an enclosed area of an anthracite mine while a fire existed therein. The Bureau men arrived at the scene of the fire, on October 27th. Dams were in place and water was being forced behind the dams in an effort to flood the fire area. The dams were placed in steep pitching chutes, and the water had to roof the chutes at the dams, and from there back up hill in order to reach the seat of the fire. Because of the pitching chutes it was difficult to make the dams hold water. Samples of the atmosphere behind the dams were obtained and analyzed. The first two analyses show the results of the first day's sampling. The two days following, despite efforts to tighten the dams, unleakage of air occurred to such an extent that the fire burst forth with renewed intensity. This happened when the oxygen in sample No. 6 had risen to 14.1 per cent. The air was inleaking through another dam, and some of the products of combustion were finding exit at the dam where sample No. 6 was collected. The air fanning the fire into a blaze probably contained about 18 per



cent. of oxygen. After sample No. 6 was taken the fire was again brought under temporary control as shown by the decrease in oxygen. The carbon dioxide and carbon monoxide also rose. Then air again started to inleak and in order to avoid another outburst of fire, a carbon dioxide fire extinguisher was brought into the mine and carbon dioxide was forced behind one of the dams for 5 hours, checking the fire until new and tighter dams could be built. The rise in carbon dioxide due to this cause is shown by sample No. 10 collected one-half hour after the use of the extinguisher had been discontinued.

No. 8 Series.

Samples of normal mine air from different sections of a mine working the Pittsburgh seam.

	Sample No.	Cu. ft. of air per min.	CO_2. %	CH_4. %	Cu. ft. of CH_4 per min.
	1	17400	0.04	0.10	0.17
	2	21600	0.06	0.94	203
Return	3	63000	0.11	0.75	473
Face	4	air still	0.12	1.80	
Return	5	79800	0.15	0.19	152
	6	21600	0.06	0.10	22
	7	31500	0.13	0.70	220
	8	air still	0.11	1.38	
	9	39200	0.15	0.75	294
	10	8100	0.09	0.34	28
	11	11400	0.06	0.14	16
	12	32400	0.09	0.94	305
	13	23200	0.05	0.95	220

Series No. 8 show the carbon dioxide and methane in the normal mine air of different parts of a large mine working the Pittsburgh coal seam. At the time the new Pennsylvania mining code was proposed, embracing certain features relating to the percentage of methane allowable, one of the mining companies asked the Bureau to sample the air in its mines with a view to determining just how much methane was present. Since that time the Bureau has trained a chemist for the work, installed a gas analysis apparatus and the company is now having daily analyses made. It can be stated that the Bureau will do this much for other mining companies if they desire closer methane determinations than the safety lamp will show. It might be mentioned that the state inspection department of Alabama, among others, is being given similar aid. The Chief Mine Inspector is installing a laboratory in his office and his men will frequently send in samples.

No. 9 Series.

Atmospheres Extinctive to Flame.

	Dry basis, Per cent.
Wolf lamp flame, bonnetted:	
CO_2	3.00
O_2	16.50
Wolf lamp, without bonnet:	
CO_2	3.00
O_2	15.82
Bunsen burner (natural gas):	
CO_2	3.25
O_2	13.90
Acetylene lamp:	
CO_2	6.30
O_2	11.70
Candle flame:	
CO_2	2.95
O_2	16.24

In these experiments, series No. 9, the different flames were placed under a 10-liter bell jar and the atmosphere analyzed after the flames had become extinguished, due to the consumption of oxygen. It might be well to call attention to the tenacity to existence of the acetylene flame. In other words it will burn in an atmosphere in which the ordinary flame cannot exist. Also that it is bad practice to work in an atmosphere deficient in oxygen to the extent any of these analyses show.

No. 10 Series.

The composition of some gas samples obtained from a mine about 18 hours after an explosion had occurred therein.

No. 1 Sample.

	Per cent.
CO_2	1.37
O_2	18.14
CO	0.60
CH_4	1.23
H_2	0.28
N_2	78.38

No. 2 Sample.

	Per cent.
CO_2	0.32
O_2	20.50
CO	0.04
CH_4	0.19
H_2	0.00 (below 0.02%)
N_2	78.95

Sample No. 1 of No. 10 series was obtained at the face of an entry by Bureau men equipped with oxygen helmets. The ventilation in this section of the entry had not been restored. The seat of the explosion was supposed to have been close to this place. A canary bird carried by an exploring party, unequipped with helmets, collapsed as it was being carried in this entry about 200 feet back from the face. The men retreated without suffering any distress. The bird revived quickly when brought back to fresh air. This particular sample is typical of those atmospheres which have caused many fatalities among rescue parties. A lamp would burn fairly well in such an atmosphere and a rescue party would have no knowledge of the presence of the deadly carbon monoxide. Canary birds carried with the party would immediately show the presence of the poisonous gas. The sample is further interesting in that 1.23 per cent. of methane was found to be present. This particular explosion was supposed by some to have been originated by the flash of short-circuited electric wires igniting coal dust, but the fact that considerable methane was found at the face, points to the possibility of fire-damp playing some part in the catastrophe.

No. 2 sample of No. 10 series was obtained in a section of the mine where ventilation had been partly restored. Even so, 0.04 per cent. of carbon monoxide was still present. Our party and others spent some considerable time in this section without feeling any effects from the white-damp, although one member stated he did not feel very well. This man had, however, been traversing this and other sections of the mine for 7 or 8 hours, consequently it is very possible that he had been breathing small

percentages of carbon monoxide a large part of the time. Eight men lost their lives in this explosion, and at least six of them were overcome by carbon monoxide. Some of the rescue party also experienced very narrow escapes from the after-damp. If they had provided themselves with canary birds in the beginning of the explosion work, it is probable that a large part of the distress experienced by them would have been avoided.

METHANE APPARATUS

Fig. 1 shows a simple gas analysis apparatus which has been assembled especially for the use of mine superintendents, foremen and inspectors. Methane can be determined with an accuracy of 0.1 per cent. in less than 10 minutes. It consists of a measuring vessel, *A*, for measuring the gas, and a burning vessel, *B*, for burning out the methane from a measured volume of mine air. *C* is the sample pipette. The mine air is drawn into the measuring vessel *A* from the pipette *C*, measured, and passed into the burning vessel *B*. The platinum wire therein is electrically heated to a white heat and allowed to remain so for 3 minutes. The current is then broken and the pipette cooled. The mine air is then drawn back into the measuring vessel and the contraction in volume due to the burning of the methane is determined by again measuring the sample. This contraction in volume when divided by 2 and calculated to a percentage basis gives the amount of methane present in the sample. The measuring vessel or burette has a total capacity of 50 cc. and is divided into the bulb at the top having a capacity of 45 cc. and the stem which has a capacity of 5 cc. The stem is graduated in 0.05 cc. or twentieths. Water is used both in the measuring and burning vessels. The apparatus works on no new principle but follows the method adopted by Coquillon, Winkler and others who burn the methane out of a measured volume of mine air.

The Bureau of Mines has assembled other types of gas analysis apparatus more accurate than the one described, but which are not simple of operation, and which are meant for the use of chemists.

SALT-RISING BREAD AND SOME COMPARISONS WITH BREAD MADE WITH YEAST.

By Henry A. Kohman.

Received October 12, 1911.

[*Concluded from the January No.*]

GASES EVOLVED.

It was observed by Clapp, as already mentioned, that when a lighted match is applied to the bubbles which form on the "emptyings" the escaping gaseous products burn. This he attributed to the evolution of alcohol. The evolving gases were determined as follows: 46 grams of cornmeal, 20 grams of powdered milk and 4 grams of starter were stirred into sufficient hot water to make a batter. After 8 to 10 hours when gas was being given off rapidly, the fermenting mass was stirred into a mixture of 1000 cc. water and 120 cc. powdered skim-milk. The meal settled to the bottom and the decanted milk was used for collecting the gas; glass cylinders of a capacity of 500 to 750 cc. were filled with this milk and inverted in a porcelain dish over a portion of the same milk. Gas began to form at once and after standing for an hour or two the cylinder was completely filled. The cylinder was half filled in about 20 to 30 minutes but as the column of liquid became shorter, the increase in volume of gas was proportionally slower. The gas obtained by this method, it was assumed, is similar to that produced in the bread.

The collected gas was taken into a 100 cc. Hempel gas burette by displacing water. The CO_2 was determined in a KOH pipette, the oxygen in a phosphorus pipette and the hydrogen by passing the gas through a short capillary tube filled with palladiumized asbestos, the tube being kept at a temperature of 100° C. In Series 1 and 2 methane was tested for by passing the gas into an explosion pipette but none was detected. The following table shows the composition of the gases.

Series 1.—Preliminary.

	Gas taken. cc.	Vol. after CO_2 removed. cc.	Oxygen added. cc.	Contraction. cc.	CO_2. Per cent.	H. Per cent.
	56.6	36.2	22.2	48.2	**36.1**	**57**

Series 2.

A.....	64.9	39.7	39.7	56.8	**38.8**	**52.2**
B.....	73.3	44.7	33.5	62.7	**39.8**	**57.0**

Series 3.

A.....	74.6	48.2	33.4	66.8	**35.4**	**60.0**
B.....	68.6	44.5	26.3	63.4	35.1	61.7

Series 4.

	Gas taken cc.	Vol. after CO_2 removed. cc.	After over P. cc.	Oxygen added. cc.	After explosion. cc.	Decrease. cc.
A.....	78.0	48.5	48.0	81.6	13.3	68.3
B.....	79.7	49.8	49.3	78.8	9.6	69.2

	CO_2 found. Per cent.	Oxygen found. cc.	Air. Per cent.	H. Per cent.	Total CO_2 + H + air. Per cent.
A.....	37.8	0.5	3.2	**58.3**	**99.3**
B.....	37.6	0.5	3.2	**58.7**	**99.5**

In Series 1 and 2 the gas used in the analyses was collected immediately upon mixing the milk and the fermenting mass. It was observed that after the cylinder was filled with gas and removed from the milk that a rennet curd had formed which was carried to the top by the evolving gas and could readily be skimmed off. In Series 3 and 4 the milk used was boiled to expel carbon dioxide and air and cooled to 45° C. before mixing with the fermenting mass, also the first cylinder of gas evolved was discarded and that used for analysis was collected over the clear whey after the curd was skimmed off. By discarding the first cylinder of gas, it was assumed that the whey became saturated with the evolving gases. The Hempel burette was filled by displacing this clear whey.

In Series 1, 2 and 3 it will be seen that the CO_2 and hydrogen never exceeds 97 per cent., and in Series 4 the oxygen was also determined after removing the CO_2. This oxygen was calculated to its equivalent of air and added to the percentages of CO_2 and hydrogen and brings the total to nearly 100 per cent. Since no methane was found, the hydrogen in Series 4 was determined by means of an explosion pipette. Each series was collected from a separate lot of the fermenting milk, and as some air is sure to be dissolved when the cylinder is filled this may account for the discrepancies in the different series.

LOSSES IN BREAD-MAKING.

In making bread with yeast it is found that best results are obtained when the dough is allowed to rise from 1 to 4 times, depending upon the "strength" of the flour, previous to moulding into loaves. During this period of fermentation which generally ranges from 5 to 8 hours in the "straight dough" process of making bread, various chemical and physical changes take place which render the gluten more elastic and better suited for the production of light bread. These changes are chiefly: (1) The formation of alcohol and CO_2 from the sugars; (2) the production of soluble carbohydrates, as sugars and dextrins, from insoluble forms as starch; (3) the production of various organic acids such as lactic, acetic and at times butyric; (4) a partial solution of the proteid compounds in the flour; (5) the formation of amid and ammonium compounds from insoluble proteins; and various other changes that are only incompletely understood. Inasmuch as many of the substances formed during the processes of fermentation are either gases or are volatile, appreciable losses of dry matter occur during the fermentation and baking of bread.

These losses as determined by various investigators are as follows: Voorhees,[1] 4.3 per cent.; Heeren,[1] 1.57 per cent.; Fehling,[1] 4.21 per cent.; Craeger,[1] 2.14 per cent.; Jago,[2] 2.5 per cent.; Danglish,[1] 3 to 6 per cent.; Snyder and Voorhees,[3] 2 to 6 per cent. or even 11 per cent. in cases of long fermentation processes.

While, with the use of yeast better bread can be made by permitting it to rise previous to moulding it into loaves, it is best to put salt-rising bread into pans at once upon mixing the dough; indeed if allowed to stand only an hour or two, marked changes occur in the physical nature of the dough and the bread becomes inferior in quality. This no doubt is to be explained by the fact that the bacteria in salt-rising bread have a greater proteolytic power than yeast in proportion to their amylolytic power. Hence the gluten is sufficiently ameliorated as soon as the gas necessary for aeration is produced. While with the use of yeast, it is found necessary to allow the dough to rise to double its original bulk several times before moulding into loaves, in order to bring about the necessary degradation in the gluten.

The difference in the methods of fermentation, the difference in the gases produced, and the absence of alcohol in salt-rising bread was suspected to make an appreciable difference in the losses of dry material in the two kinds of bread. It was observed, too, both by the author and practical bakers, that the yield in salt-rising bread is invariably somewhat larger than in yeast bread.

With the object in view of detecting any differences that normally occur in the losses of these two types of bread, these were determined. The flour used was a Kansas patent and the bread was fermented as nearly as possible in accordance with the best bakery practice. All determinations were made from the same sample of flour. This was made uniform by putting about equal portions in eight separate dishes and then partly filling a large glass stoppered bottle from these by taking in rotation a tablespoonful at a time from each dish. When the large bottle was about two-thirds filled, it was rolled back and forth over the floor so as to insure perfect uniformity.

The yeast bread was made by the straight dough process which is used most extensively by manufacturing bakers at the present time.

The bread was mixed in a small universal bread mixer as it was found that there was less mechanical loss than if mixed by hand. The yeast was dissolved in a small portion of the water and the salt and sugar were put into the mixer and dissolved in a part of the water. The yeast was then added and the containing vessel rinsed with the remainder of the water. The flour was then put in and the mixer turned, until the dough was uniform, when it was carefully removed and put into a large porcelain evaporating dish and allowed to ferment as long as had previously been determined best for this particular flour. It was kneaded down three times. After having been properly fermented the dough was moulded into 2 loaves, without the use of flour, allowed to rise and baked regularly in an electric oven at a temperature of 220° to 230° C. It was thought best to use as large quantities as given above, for it was a convenient amount for the mixer and can be handled with a smaller percentage error, due to mechanical losses than a smaller amount. It was found that a little material remained both in the mixer and the evaporating dish in which the dough was fermented. That in the mixer was estimated by allowing it to dry in the air and then weighing the mixer on a torsion balance both before and after the mixer was washed out and dried thoroughly. The difference was small, less than $^1/_{10}$ of 1 per cent. of the total quantity of flour used and was deduced from this amount. That in the evaporating dish was dried in a large copper water-jacketed oven and then calculated from the difference in weight of the dish before and after washing and drying. This amount was also small and was deduced from the total amount of dry material used.

In these experiments no attempts were made to determine the nature of the losses in bread-making but merely the absolute amounts. The two loaves were baked side by side in a single pan, and in sampling they were broken apart and each loaf was cut into four nearly equal pieces. An end piece of one loaf and the diametrically opposite center piece of the

[1] U. S. Dept. Agr., Office of Experiment Stations. *Bull.* **35.**
[2] Jago, "The Science and Art of Bread-Making," p. 361.
[3] U. S. Department Agriculture, *Bull.* **67,** pp. 11 and 28.

other loaf were taken as an aliquot part of the total weight of the bread. These were dried sufficiently to be crumbed by means of a small coffee mill and separate small portions of 2 to 3 grams were used in drying completely in a water-jacketed oven. It was found difficult to get concordant results by drying small portions of the crumbs although they were thoroughly mixed; and also that the pieces as chosen above did not represent a true sample of the baking and this method of determining the moisture in the bread was abandoned. The losses as determined by this method varied as widely as 4.88 per cent. to 6.79 per cent. in two different bakings made as nearly alike as possible. On another occasion a variation of from 7.3 per cent. to 9.7 per cent. was obtained. As it was impossible to obtain concordant results by drying samples, the whole quantity of bread in each baking was dried in a large water-jacketed oven. The bread was cut in thin slices, care being taken that no crumbs were lost, and placed loosely in large porcelain dishes and dried. After drying it was cooled in large desiccators over sulphuric acid and weighed on a torsion balance, upon which all the ingredients as well, were weighed. By this method a constant weight could be obtained and the results obtained from separate bakings by the same method were concordant.

In addition to determining the losses in bread fermented normally with yeast, they were also determined when the dough was moulded into loaves and placed into pans at once upon mixing without previously allowing it to rise. When it had risen to the usual height it was baked, dried and weighed as described above. The losses in salt-rising bread were determined in practically the same way except that the bread was made by the sponge and dough method which is commonly used for this type of bread. The amounts of ingredients used are as given in baking No. 378, and the time and temperature of mixing "emptyings" then determined as was done with yeast bread and subtracted from the amount of flour used.

The moisture in the ingredients used in these experiments was determined by careful sampling and drying small separate portions in the water-jacketed oven. As the moisture content of the flour the mean of 6 closely agreeing determinations was used, while the moisture content of the other ingredients was determined only in duplicate. The salt was heated until decrepitation ceased and was then assumed to be free from water. Knowing the amounts of ingredients used, the percentage of moisture in each and the weight of dry material recovered the loss of dry material can be readily calculated.

The materials used in making the breads are given in the following table:

MATERIALS IN BREAD MADE WITH YEAST.

Fermented normally.	Flour. Grams.	Water. Grams.	Yeast. Grams.	Sugar. Grams.	Salt. Grams.
Bread No. 99.....	800	490	10	12	12
Bread No. 100.....	800	490	10	12	12
Put into pans at once upon mixing.					
Bread No. 101.....	400	245	5	6	6
Bread No. 102.....	400	245	5	6	6

SALT-RISING BREAD.

	Flour.	Water.	Corn-meal.	Salt.	Milk.	Soda.	Starter.
Bread No. 378.....	800	550	22	12	5	2	2
Bread No. 381.....	800	550	22	12	5	2	2

The losses expressed in percentages, as given in the table, are calculated upon the total dry material used in each baking and it will be observed that they are much smaller in salt-rising bread than in bread made with yeast, and that in the latter they depend upon the amount of fermentation the bread is subjected to.

Breads No. 101 and No. 102 were of poor quality, being coarse in texture and dark in color as is always the case when bread made with yeast is not allowed to rise several times previous to putting into pans. Over three hours were required for the bread to rise to the usual height in the pans while ordinarily, when the bread is fermented in the usual way, it rises in 35 to 55 minutes. It was made by this method merely to show that the losses are due largely to the destruction of materials by the yeast. The losses in salt-rising bread were found to be even smaller than in sponge and dough as well. The small portion of the ingredients that remained in the beaker and evaporating dish from the "emptyings" and sponge respectively was determined by drying in the water-jacketed oven and weighing on the torsion balance both before and after washing and drying. This amount was small in proportion to the total quantity of ingredients and was deduced from the total dry material used. What remained in the bread mixer was air dried and

LOSSES IN BREAD-MAKING.

Materials (water-free).

Bread made with yeast: Fermented normally:	Flour. Grams.	Yeast. Grams.	Sugar. Grams.	Salt. Grams.	Material used (dry). Grams.	Material recovered. Grams.	Material lost. Grams.	Loss. Per cent.
Bread No. 99	711.34	3.65	14.99	12.00	741.98	704.95	37.03	4.99
Bread No. 100	711.53	3.65	14.99	12.00	742.17	702.75	39.42	5.31
							Mean,	5.15
Put into pans at once upon mixing:								
Bread No. 101	356.30	1.82	7.49	6.00	371.61	365.25	6.36	1.71
Bread No. 102	356.29	1.82	7.49	6.00	371.60	364.50	7.10	1.91
							Mean,	1.81
Salt-rising bread:	Flour.	Salt.	Cornmeal.	Soda.				
Bread No. 378	710.84	12.00	19.80	1.95	751.27	748.20	3.07	0.41
Bread No. 381	710.34	12.00	19.80	1.95	750.77	747.00	3.77	0.46
							Mean,	0.44

	Milk.	Starter.
378	4.82	1.85
381	4.82	1.85

bread made with yeast when allowed to ferment merely enough for aeration.

This difference in the losses in the two types of bread is to be explained by the fact that: (1) yeast produces 1.04 parts of alcohol for every part of CO_2, both of which are largely driven off during the process of baking, while in salt-rising bread there is no alcohol produced; (2) it is necessary to ferment bread with yeast from 5 to 8 hours while it is allowed to rise in the pans only one hour or less, hence only a small part of the total gas produced is actually used in aeration, while salt-rising bread is made into loaves at once upon mixing the dough and very little gas is lost; (3) the gases produced by yeast consist of CO_2, while those produced by the salt-rising bacterium consist of about $^1/_3$ CO_2 and $^2/_3$ hydrogen which is only $^1/_{22}$ as heavy as the former.

The fact that the losses in ordinary bread vary with the amounts of fermentation perhaps in part accounts for the variation in the results obtained by different investigators. Snyder allowed the dough to double its bulk only once and baked it after it rose again, which by practical bakers would be considered sufficient fermentation only for very weak flours such as are generally used in making pastries. Losses of 8.14 per cent. and 10.23 per cent., as reported in *Bull.* **67,** U. S. Dept. Agr., p. 28, it is the opinion of the author, are due to experimental errors, for the flour used in these experiments required and was subjected to more than the average amount of fermentation, and the 5.15 per cent. is considered more than an average loss.

The fact that the bacteria in salt-rising bread by their presence in the dough have such a marked effect upon the gluten and that best results are obtained by placing the loaves into pans at once upon mixing the ingredients is considered significant and an effort was made to produce the same results in yeast bread by adding various agents such as other bacteria, enzymes and organic acids.

Cream of tartar when added to the usual ingredients produced a shortening effect upon the dough and hence it was not necessary to subject it to the same amount of fermentation. It was not possible, however, to produce bread with good color and texture by moulding the loaves as soon as the dough was made even though sufficient acid was used to render the dough short to the feel. In excess acids weaken flour and smaller and poorer loaves are the result.

Pepsin was added to doughs in the proportions of 0.1 gram, 0.2 gram, 0.5 gram and 1.0 gram to 800 grams of flour, and it was found that in all cases it was necessary to give the bread a preliminary rising before putting into pans. When pepsin was added to the extent of $^1/_8$ of 1 per cent. the dough became runny and sticky in a short time and it was impossible to make good bread from it, either when it was moulded into loaves at once or when previously allowed to rise. The bread was extremely coarse and darker in color, and at times the destruction of the gluten was made evident by the formation of a large hole extending almost the whole length of the loaf. In all cases, even when only 1 part to 4,000 parts of flour was used, the pepsin produced a noticeable effect. The dough invariably became more runny and the loaves flattened somewhat, and it was questionable whether it was of any advantage even in extremely small quantities. When used to the extent of 1 part in 1600 parts of flour, its effect was harmful without a doubt.

Five different malt extracts which contain both amylolytic and proteolytic enzymes were used in an effort to hasten the changes that are necessary in dough to make it suitable for bread-making purposes. The activities of these extracts were found to be as follows: No. 1, 8.56; No. 2, 15.71; No. 3, 8.69; No. 4, 9.69; No. 5, 20.13. The activity is defined as the number of times its weight of maltose a given quantity of extract will produce when allowed to act upon an excess of acid-free soluble starch for one hour at a temperature of 40° C.

Various baking experiments using these extracts in different porportions indicate that the extracts have a marked proteolytic action as well as sugar-producing powers. The stronger extracts, especially when used in quantities exceeding $^1/_2$ or 2 per cent. calculated on the flour, have a decided softening action upon the dough, which seems similar to that produced by pepsin. Flour made from wheat that has germinated has a tendency to soften and become "runny" which would indicate the development of proteolytic enzymes. These experiments with malt extracts indicate that while they have an action upon the gluten and shorten the period of fermentation somewhat, their function in bread-making is mainly amylolytic. When used in bread-making they produce considerable sugar as may be seen from the following results obtained by the author.

SUGAR IN BREAD.

Bread No.	Saccharine material added.	Sugar found. Per cent.
1	$2^1/_2$ cane sugar.	5.37
2	None.	3.64
3	1 per cent. extracted No. 5.	6.00
4	1 per cent. extracted No. 1.	5.68
5	$^1/_8$ of 1 per cent extracted No 5 and $3^1/_2$ per cent. cooked flour.	5.27

The percentages of saccharine material added are calculated on the flour, and the percentages of reducing sugar found are calculated as maltose on the water-free bread.

It is well known that dough is a suitable medium for bacterial growth and as, in these experiments, one culture was isolated that could both aerate bread and produce the necessary transformations in the gluten, an effort was made to couple the gas-producing power of the yeast with a bacterial fermentation that would quickly bring about these later changes and perhaps also have an important bearing upon the flavor of the bread.

Preliminary experiments were made to determine the number of bacteria normally present in flours. These were found to vary in numbers from about 25,000 to 300,000 cells per gram of flour. Bleached

flour from the same sample of wheat was found to contain only about $^1/_2$ to $^3/_4$ as many as the unbleached.

Two of the commoner bacteria found in flour were isolated and the pure cultures used in various experiments in bread-making. For convenience they will be designated as A and B. When grown in milk A produced a soft white curd which did not separate from the whey even after standing several months. B produced more acid and after standing a few weeks the curd was almost completely dissolved, forming a dark colored solution. Bread was made by adding milk in various proportions, which had been fermented from 40 to 72 hours with these bacteria. A had no marked effect upon the feel of the dough and the bread was normal except that it was closer-grained and the loaves had a tendency to crack. The dough made with the addition of B was stickier, softer and more runny than usual, although no more than the usual amount of water was added. The bread was smaller in volume and had still more tendency to crack. In these experiments it was found that the effect of the bacteria depended largely upon the activity of the yeast. If the yeast was used sparingly or if it was weak and the bacteria were added in large numbers the effects enumerated above were quite pronounced, while if plenty of strong yeast was added, even in the presence of many bacteria, the bread was nearly normal. In one series of experiments normal bread was made from a flour containing 26,000 bacteria per gram, by adding enough milk, fermented with A to increase that number 30,000-fold, and with B to increase the number of cells 60,000-fold.

Besides these baking experiments with pure cultures a series of bakings was made using buttermilk as part of the liquid. The buttermilk was used in proportions ranging from $^1/_5$ to $^4/_5$ of the total liquid used and in all cases it was found that it had a softening action upon the dough. The bread was smaller in volume and firmer than when no buttermilk was added and had a tendency to crack near the top edge of the pan. Even though the bacteria exceeded by ten-fold or more the number of yeast cells present in the dough, it was found advantageous to allow the bread to rise and to knead it down previous to molding the loaves. If the yeast was strong and produced a vigorous fermentation the effect of the bacteria was not marked and these experiments would indicate that, while sour bread was formerly a common occurrence, in the modern short fermentation processes bacteria play a less important role than is supposed and that flavor in bread is to be attributed rather to the activities of the yeast than to bacterial fermentation.

While neither the pure cultures of bacteria obtained from flour nor the bacteria in buttermilk had sufficient action upon the gluten to permit molding into loaves at once, it was possible to make a dough, using a salt-rising sponge and compressed yeast, and put the loaves into pans at once upon mixing with good results; indeed the bread was better in texture than if it was allowed to rise before molding into loaves. With the use of other bacteria, together with compressed yeast, on the other hand, better bread could be made by allowing it to rise once or twice before molding. While the use of compressed yeast in salt-rising bread produces good-appearing bread with good texture it has not met with the approval of the consumer, for it loses more or less of its characteristic taste and acquires another due to the yeast. On theoretical grounds it would hardly be expected that the two organisms can be used to advantage in the same dough for the production of bread, owing to the great difference in temperature at which they work best. It is in accordance with the best bakery practice to-day to ferment doughs with yeast at a temperature of 26° C. while the optimum temperature for the salt-rising organism lies about 15° C. higher.

Some of the bacteria normally present in cornmeal are extremely resistant to heat, so much so that a mixture of meal and milk, after being steamed for two hours or for a half hour on three or four successive days, will at times show the evolution of gas after incubation.

The artificial product prepared in these experiments is even more resistant to heat and shows the evolution of gas much sooner as may be seen from the following experiment: into 250-cc. German flasks containing 150 cc. water, which was brought to a boil, were stirred, in Series 1, 18 grams of cornmeal and 10 grams dried skimmed milk, and in Series 2, 18 grams of the artificial product and 10 grams of the same milk.

Series 1.	Series 2.	Time steamed.
Flask No. 1*a*	Flask No. 1	1 hour
Flask No. 2*a*	Flask No. 2	1 hour and 20 min.
Flask No. 3*a*	Flask No. 3	1 hour and 40 min.
Flask No. 4*a*	Flask No. 4	1 hour and 55 min.

The flasks were plugged with cotton and immediately placed in a steaming autoclave. After being incubated at 40° C. for 18 hours, all flasks in Series 2 were giving off gas while in Series 1 no signs of life were evident within 48 hours when a few gas bubbles began to form in flask 1*a*. No gas appeared in flasks 2*a*, 3*a* and 4*a* even after incubating for 3 days, although putrefaction set in.

In another series 6 flasks were made as in Series 2 and heated respectively 1 hour and 55 minutes, 2 hours and 25 minutes, 2 hours and 55 minutes, 3 hours and 25 minutes, 3 hours and 55 minutes, and 4 hours and 30 minutes. Flasks 1, 2 and 3 were evolving gas after incubating for 18 hours; flask 4, 2 hours later; while flasks 5 and 6 became putrid after three days.

This treatment is far more severe than any the organisms are subjected to in the process of baking the bread, and Dr. Emley raised the question whether or not they survive the heat of the oven and perhaps cause disturbances, due to gas production, in the alimentary tract of the consumer. To throw some light upon this question some of the bread was cut at various times with a sterile knife, and small portions of about 1 gram each were plucked out from the freshly cut surface with a sterile pair of forceps and dropped into test tubes partly filled with sterile milk. This was done repeatedly, and of all the tubes inocu-

lated in this way only about one-half showed any growth. The growth was seldom observed in less than 24 hours and in no case did gas bubbles appear as is always the case when sterile milk is inoculated from the fermenting batter, which would indicate that the gas-forming organisms perish in the oven. The fact that these organisms do not survive in the bread when it is in the oven only about 45 minutes and reaches a temperature of 100° to 103° C. for only a few minutes, and yet in a batter made from meal and milk are not killed by three hours' steaming, can be explained only by differences in the life history of the organisms. In the meal they occur as spores while in the bread they are actively growing and are quickly killed by the heat before they can pass into the more resistant state. The organisms that do survive are probably introduced as spores by means of the flour rather than the meal, for in the former they have much the shorter time to germinate. This is supported by the fact that salt-rising bread keeps as well as bread made with yeast, and that the latter also is not an absolutely sterile product for certain organisms that cause ropiness in bread are known to survive.

The flora of bacteria present in the fermenting salt-rising batter made from cornmeal varies greatly, depending upon the temperature that obtains when the meal is stirred into the water or milk. If the temperature of the mass does not exceed a temperature of about 65° an organism or perhaps a group of organisms may be isolated that will produce gas readily in milk or broth or even on plates unless they are very shallow. When grown in nutrient agar it produces gas also and causes holes and rents in the medium. On plates it appears in round, raised, semitransparent colonies. In milk gas bubbles are given off and after about two days, sometimes less, a curd will form which is broken and full of gas bubbles. After a week or longer a part of the curd, usually down one side of the tube, will dissolve, leaving a clear light colored whey. In broth gas bubbles are given off and a rather uniform cloudiness appears. In stab cultures the growth spreads over all or nearly all the top of the medium, while farther down gas bubbles appear. The growth along the line of puncture is rather feathery, disturbed or broken by gas bubbles here and there. Stroke cultures show an abundant raised growth semitransparent, with smooth projections extending out. On potato a narrow raised, grayish white growth appears, which does not show a tendency to spread. Gelatin is not liquefied at room temperature, and if incubated at 37° C., will solidify again on cooling. It forms indol. If the temperature of the batter exceeds 75° C. this organism is not found upon plates poured from it, and spore formation has not been observed. These cultural characteristics together with its morphology and staining properties indicate that it is a member of the coli group.

Another colony which was more opaque and slightly ragged also produced gas in milk but produced no curd within four days. The curd was more broken with gas bubbles than when the milk was fermented with the other culture. In their growth in stab and slant cultures the two could not be distinguished, but on potato this last one described produced a creamy, yellowish growth instead of a grayish white. It is probably a member of the same group.

In addition to these, certain flat, white, opaque colonies, with ragged edges, appeared in about equal members. These also produced gas in small quantities and formed a curd when grown in milk. Also certain flat, smooth-edged, opaque colonies were evident. None, or very few indeed, of the colonies that appear upon milk-agar plates poured from batters, the initial temperature of which did not exceed 60 to 65° C., show a peptonization of the milk either upon the plates themselves or when transferred to milk tubes. If the temperature of the batter exceeds 75° C., however, a different flora of bacteria is present, for nearly all the colonies that appear show a peptonization of the milk, which is made apparent by the clear zone that surrounds the colonies, and also by the yellow solution that is formed when the colonies are transferred to milk tubes. The bacteria that survive the higher temperatures differ also in that they, as far as has been determined, liquefy gelatin. If a temperature of 75° C. or over obtains in making the batter, it is only occasionally that gas bubbles appear in plates made from it although the batter itself is vigorously evolving gas, and, as already stated, only once, and then not without some doubt in regard to its purity, was a culture obtained that would produce gas, and this culture soon lost this ability. When the meal is subjected to lower temperatures, however, a gas-forming organism can readily be isolated, and it is the opinion of the author that the pure culture with which bread was made in these experiments was subjected to a temperature lower than 75° C., by the housewife making the bread, and that the organism, although its cultural characteristics were not fully determined, was a member of the coli group. It produced a similar reaction in milk and gelatin media, did not form spores, and had the morphological characteristics.

As would be expected from the variations in the flora of bacteria present in the batter, depending upon the temperature at which it is made, differences are also observed in the character of the bread produced. The batter when not subjected to temperatures that destroy non-spore-bearing organisms has a different and usually a stronger odor which at times becomes very offensive, and it not eliminated during the process of baking, although it is usually moderated somewhat. It is the experience of the author that better bread is obtained if the liquid used in making the batter is brought to a boil, which subjects the meal to a temperature of 85 to 90° C., than if the batter is set at lower temperatures. Fermentation and the evolution of gas begins sooner, but with less regularity and certainty, when the temperature of the batter is not raised to the point at which non-spore-bearing organisms perish. With the use of the artificial product prepared in these experiments, however, which it was found best to stir directly into the boiling liquid,

the evolution of gas begins both sooner and with a much greater degree of regularity than if meal is used and set at the most favorable temperature.

CONCLUSIONS.

The leaven in salt-rising bread is not yeast as is indicated by the literature on the subject, but certain bacteria. These bacteria aerate the bread by decomposing certain of its constituents, principally the sugars, into gaseous products and not, as has been suggested, by producing acids which liberate carbon dioxide from the soda. The microbic flora involved varies greatly, depending upon the temperature to which the meal is subjected in setting the "batter." The organisms that predominate in the batter when it is made by stirring the meal into boiling milk or water are only occasionally found upon plates made from batters that were not subjected to temperatures which destroy non-spore-bearing organisms. The chief source of the bacteria is not the air and utensils, as has been suggested in the literature, but the corn-meal used in making the batter. One organism was isolated which in pure culture produces the gas necessary to properly aerate bread. This bacterium seems to be a member of the coli group and was never found in batters that were heated to 75° C. It in all probability belongs to the same group as the organism described by Wolffin and Lehman, which they call *Bacillus levans*. This organism could be propagated in liquid media, such as milk, or could be grown in a batter and subsequently dried, to be used in the preparation of bread.

When the liquid used in making the batter is taken sufficiently hot to bring the temperature of the batter to 75° C. or higher, certain spore-bearing organisms prevail which readily produce the gas necessary to aerate bread. These bacteria soon lose their gas-producing power when kept in liquid media or when transferred to fresh media at intervals of 12 or 24 hours. From this fermenting batter no culture was isolated that retained its ability to produce gas when kept in the liquid state. A dry product consisting for the most part of starchy material was prepared, however, which could be used at will in making uniform bread.

Bread made by the "Sauerteig" method differs from salt-rising in that the gaseous fermentation in the latter is due entirely to bacteria, while in the former the leavening power owes its origin primarily to yeasts, and it is a question whether the bacteria present, some of which are gas formers, are desirable or not; they differ also in that the latter is made from fresh material each time, while in the preparation of the former a portion of dough is saved to start the fermentation in the next baking.

The gases produced by the salt-rising bacteria, as found in these experiments, consist of nearly $^2/_3$ hydrogen and rather more than $^1/_3$ carbon dioxide and no hydrocarbons.

The losses of materials, due to decomposition and volatilization of some of the constituents, are much smaller in salt-rising bread than in bread made with yeast, and the losses in the latter vary with the amount of fermentation to which it is subjected. This difference in the losses of materials in the preparation of the two kinds of bread is to be explained by the fact that (1) there is no alcohol found in the former; (2) that owing to inherent difference in the nature of the ferments involved it is subjected to far less fermentation; and (3) the gases are much lighter.

The author wishes to express his gratitude to Robert Kennedy Duncan for his helpful advice and direction in this work.

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A STUDY OF THE VISCOSITY OF FISH OILS.

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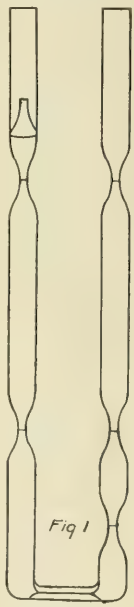
Received November 8, 1911.

Up to the present, the measurement of the viscosity of oils has been carried out by means of the Ostwald viscosimeter, and also by means of various commercial instruments which are unsuitable for scientific research, although possessing an ease of manipulation very desirable in this work. The former instrument has been shown to have only a limited degree of exactness[1] which is not great enough to obtain the relations between the viscosity of liquids and other physical or chemical properties and establish them on a firm basis. Bingham and White[2] have described a viscosimeter capable of measuring viscosity with the greatest accuracy, by which absolute results are obtained; that is, a constant amount, of liquid is passed through a capillary tube of known diameter and length, the time of flow being regulated by a variable pressure which is adapted to the nature of the liquid. Recently the author[3] of this paper has devised an instrument of the same general type which can be readily constructed and also is quite exact. The calibration of the viscosimeter, the method of manipulation, and data showing its accuracy were presented in the previous article; also it was used to measure the viscosity of blood and blood serum and was found to be generally applicable for that work.



VISCOSIMETER B

In this investigation the viscosimeter[4] A, which was referred to above, was modified for the measurement of the viscosity of fish oils, which of course are relatively very viscous compared with water and aqueous solutions. The same method of procedure was followed in this work as in that with blood and blood serum, a known volume of liquid passing through a capillary tube of known dimensions under a

[1] Schmidt, dissertation, Baltimore, Md., 1909. Bingham and Durham, *Am. Chem. J.*, **46**, 278 (1911).

[2] *J. Am. Chem. Soc.*, **33**, 1257 (1911). A more detailed description will soon be published.

[3] *Biochem. Z*, **37**, 482 (1911).

[4] *Ibid.*, **37**, 483 (1911).

given pressure and temperature. A new viscosimeter, B (Fig. 1), was constructed on the plan of the previous one, but with a much shorter capillary tube and with the volumes of the limbs considerably less. The method of standardizing the instrument was similar to the standardization of A in principle but water could not be used as the time of flow would be too short under the lowest pressures obtainable. Therefore, the viscosity of a sample of menhaden oil[1] was determined in viscosimeter A (which had been standardized with water), the temperature being 50° to reduce the time necessary for measurement. The viscosity was found to be 0.1518 in the left limb and 0.1514 in the right limb—average 0.1516 at 50°. Viscosimeter B was now calibrated with the above oil, and the following are the constants obtained for this instrument:

Length of capillary (approx.)	1.7 cm.
Volume of left limb	2.1310 cc.
Volume of right limb	2.0748 cc.
Pressure correction, left limb	1.23 cm.
Pressure correction, right limb	1.20 cm.
Ratio of r^4 to l	0.00004577
	0.00004582

This viscosimeter was found to give excellent results, the time of flow under a pressure of 100-180 cm. varying with the different oils from two to six minutes, depending on the nature of the oil and the temperature.

The kinetic energy correction $\frac{vd}{8\pi tl}$ in the formula

$$\eta = \frac{\pi r^4 pt}{8vl} - \frac{vd}{8\pi tl}$$

was low, this being necessary if the work is to be made as accurate as possible. This correction was always less than 0.5 per cent. of the total viscosity. In the above equation η is the viscosity, r and l are the radius and length of the capillary tube, v is the volume of liquid of density d, p is the pressure, and t is the time of flow.

Viscosimeter B was tested at 60° with the menhaden oil, the viscosity of which had been measured in viscosimeter A, and the following results were obtained:

Viscosity of Menhaden Oil.

	Rt. limb.	Left limb.	Av.
Viscosimeter A	0.1169	0.1168	0.1169
Viscosimeter B	0.1170	0.1166	0.1168
Viscosimeter B	0.1164	0.1165	0.1165

The average of the four measurements in B, 0.1167, is in satisfactory agreement with the result obtained with the other viscosimeter, 0.1169.

In general, the oils used for this investigation were extracted from fish obtained at Woods Hole, except the samples of cod, whale, and sperm oils, which were commercial products. The entire fish or the fish livers, according to the oil desired, were subjected to steam pressure in an autoclave at 115° for 2-4 hours and then filtered while hot through cloth with the aid of pressure. This separated the oil and water from the great quantity of proteid matter present, and allowed the oil to rise in a clear layer to the top of the mixture placed in large cylinders. Water was added to bring the oil to the top of these latter, and the oil was siphoned off, allowed to cool, and dried with calcium chloride for several days. The dried oil was then filtered from the salt and separated stearin or other insoluble fats through filter paper with the aid of suction, and preserved in a cool place for the resulting measurements.

The oils generally varied in color from a very light yellow to a light brown. In order to check up their composition a few constants were determined—the iodine number (Hübl), the acid number (milligrams of potassium hydroxide required to neutralize one gram of oil), and the saponification number (milligrams of potassium hydroxide necessary for one gram of oil).

Table I.

Kind of oil.	Iodine No.	Acid No.	Saponification No.
Menhaden I (commercial)	168.6	...	...
Menhaden II (dark)	128.1	6.83	16.26
Menhaden III (light)	143.3	0.88	191.1
Whale (commercial)	156.6	6.70	192.8
Cod liver (white, commercial)	142.6	1.82	185.8
Cod liver (brown, commercial)	150.9	9.83	189.8
Sperm (commercial)	85.5	0.33	167.0
Dogfish	135.9	0.94	193.0
Dogfish liver I	118.2	3.49	188.1
Dogfish liver II	124.8	1.60	189.9
Dogfish liver III	53.9	1.96	189.4
Spiny dogfish liver	142.7	4.84	171.4
Sand shark liver	213.6	1.52	182.7
Hammer-head shark liver	155.5	3.32	174.1
Torpedo liver I	111.0	0.92	164.0
Torpedo liver II	92.8	0.75	160.9
Squeteague	103.9	7.40	196.5
Scup	117.3	16.73	188.9
Butter-fish	91.1	62.07	191.4
Eel	117.4	1.02	191.1

In the following tables are given figures showing the viscosity of the oils as measured in the right and left limbs of the viscosimeter at 30°, 50°, 70°, and 90°, with the average of these at each temperature respectively, and with the corresponding fluidity. The specific gravity, as measured in the ordinary Ostwald pycnometer, is also given, as it was necessary for obtaining the kinetic energy correction involved in the formula for the calculation of the viscosity. The bath containing the viscosimeter was a large beaker of water well stirred by a suitable stirrer. The temperature was regulated by hand since the time of measurement at any one temperature was so brief as to make an automatic regulator troublesome. The temperature was kept constant to 0.02°, and great care was exercised to insure this, the temperature coefficients of viscosity of these oils being very large.

Table II.—Menhaden I, Commercial (*Brevoortia tyrannus*).

Temp.	Viscosity. R. L.	L. L.	Av.	Fluidity.	Sp. gr.
30°	0.2958	0.2965	0.2961	3.377	0.9177
50°	...	...	0.1516	6.597	0.9076
70°	0.09559	0.09551	0.09555	10.47	0.8931
90°	0.06357	0.06343	0.06350	15.75	0.8798

[1] This sample of oil, among others, was furnished by Mr. J. F. Goode, with the firm of Marden, Orth & Hastings, Boston, Mass., whose favor is gratefully acknowledged.

TABLE III.—MENHADEN II (DARK).

Temp.	Viscosity R. L.	L. L.	Av.	Fluidity	Sp. gr.
30°	0.6012	0.6028	0.6019	1.661	0.9371
50°	0.2936	0.2938	0.2935	3.407	0.9234
70°	0.1683	0.1683	0.1683	5.945	0.9097
90°	0.1097	0.1096	0.1097	9.107	0.8965

TABLE IV.—MENHADEN III (LIGHT).

30°.....	0.3243	0.3233	0.3238	3.088	0.9230
50°.....	0.1727	0.1727	0.1727	5.790	0.9090
70°.....	0.1048	0.1049	0.1049	9.533	0.8454
90°.....	0.07101	0.07092	0.07097	14.09	0.8824

TABLE V.—WHALE, COMMERCIAL (*Balaena mysticetus*).

30°.....	0.3493	0.3477	0.3485	2.859	0.9192
50°.....	0.1818	0.1824	0.1822	5.489	0.9063
70°.....	0.1103	0.1099	0.1101	9.090	0.8912
90°.....	0.07243	0.07328	0.07241	13.81	0.8782

TABLE VI.—COD LIVER, WHITE (*Gadus callarias*).

30°.....	0.3886	0.3882	0.3884	2.575	0.9277
50°.....	0.2001	0.2005	0.2003	4.992	0.9149
70°.....	0.1187	0.1189	0.1188	8.418	0.9008
90°.....	0.07862	0.07882	0.07872	12.71	0.8900

TABLE VII.—COD LIVER, BROWN (COMMERCIAL).

30°.....	0.3924	0.3924	0.3924	2.549	0.9162
50°.....	0.2078	0.2080	0.2079	4.810	0.9034
70°.....	0.1196	0.1194	0.1195	8.368	0.8911
90°.....	0.07866	0.07843	0.07855	12.73	0.8769

TABLE VIII.—SPERM, COMMERCIAL (*Physeter macrocephalus*).

30°.....	0.3333	0.3333	0.3333	3.00	
50°.....	0.1719	0.1721	0.1720	5.814	
70°.....	0.1039	0.1037	0.1038	9.636	
90°.....	0.06647	0.06662	0.06655	15.03	

TABLE IX.—DOGFISH (*Mustelus canis*).

30°.....	0.4319	0.4319	0.4319	2.315	0.9185
50°.....	0.2133	0.2138	0.2135	4.682	0.9057
70°.....	0.1262	0.1259	0.1261	7.931	0.8932
90°.....	0.08272	0.08293	0.08283	12.08	0.8796

TABLE X.—DOGFISH LIVER I.

30°.....	0.4089	0.4103	0.4096	2.441	0.9160
50°.....	0.2069	0.2075	0.2072	4.826	0.9016
70°.....	0.1213	0.1211	0.1212	8.251	0.8884
90°.....	0.07971	0.07973	0.07972	12.55	0.8758

TABLE XI.—DOGFISH LIVER II.

30°.....	0.3761	0.3762	0.3762	2.659	0.9164
50°.....	0.1977	0.1977	0.1977	5.059	0.9038
70°.....	0.1161	0.1160	0.1161	8.614	0.8902
90°.....	0.07750	0.07729	0.07740	12.92	0.8768

TABLE XII.—DOGFISH LIVER III.

30°.....	0.3781	0.3771	0.3776	2.649	0.9162
50°.....	0.1944	0.1941	0.1943	5.147	0.9128
70°.....	0.1155	0.1153	0.1154	8.666	0.8876
90°.....	0.07648	0.07628	0.07638	13.09	0.8750

TABLE XIII.—SPINY DOGFISH LIVER (*Squalus acanthias*).

30°.....	0.4000	0.3986	0.3993	2.504	0.9187
50°.....	0.2045	0.2053	0.2049	4.880	0.9074
70°.....	0.1213	0.1215	0.1214	8.237	0.8945
90°.....	0.07965	0.07949	0.07957	12.56	0.8820

TABLE XIV.—SAND SHARK LIVER (*Carcharias littoralis*).

30°.....	0.3675	0.3680	0.3678	2.719	0.9262
50°.....	0.1943	0.1942	0.1943	5.150	0.9135
70°.....	0.1177	0.1176	0.1177	8.497	0.9005
90°.....	0.07916	0.07916	0.07916	12.63	0.8867

TABLE XV.—HAMMER-HEAD SHARK LIVER (*Sphyrna zygaena*).

30°.....	0.5479	0.5461	0.5470	1.828	0.9245
50°.....	0.2682	0.2684	0.2681	3.730	0.9122
70°.....	0.1534	0.1539	0.1537	6.507	0.8986
90°.....	0.09787	0.09800	0.09794	10.21	0.8863

TABLE XVI.—TORPEDO LIVER I (*Tetranarce occidentalis*).

Temp.	Viscosity. R. L.	L. L.	Av.	Fluidity	Sp. gr.
30°.....	0.4257	0.4269	0.4263	2.345	0.9044
50°.....	0.2134	0.2131	0.2133	4.688	0.8923
70°.....	0.1256	0.1258	0.1257	7.956	0.8762
90°.....	0.08071	0.08075	0.08073	12.39	0.8676

TABLE XVII.—TORPEDO LIVER II.

30°.....	0.4775	0.4773	0.4774	2.094	0.9018
50°.....	0.2356	0.2356	0.2356	4.244	0.8890
70°.....	0.1381	0.1377	0.1379	7.252	0.8764
90°.....	0.08756	0.08746	0.08751	11.43	0.8644

TABLE XVIII.—SQUETEAGUE (*Cynoscion regalis*).

30°.....	0.4975	0.4985	0.4980	2.008	0.9177
50°.....	0.2405	0.2399	0.2402	4.164	0.9048
70°.....	0.1382	0.1385	0.1384	7.225	0.8910
90°.....	0.08904	0.08914	0.08099	11.22	0.8784

TABLE XIX.—SCUP (*Stenotomus chrysops*).

30°.....	0.4193	0.4197	0.4195	2.384	0.9168
50°.....	0.2138	0.2143	0.2141	4.671	0.9040
70°.....	0.1239	0.1239	0.1239	8.071	0.8910
90°.....	0.08129	0.08119	0.08124	12.31	0.8740

TABLE XX.—BUTTER-FISH (*Poronotus tricanthus*).

30°.....	0.4274	0.4257	0.4266	2.344	0.9090
50°.....	0.2092	0.2091	0.2092	4.780	0.8962
70°.....	0.1194	0.1193	0.1194	8.375	0.8824
90°.....	0.07624	0.07602	0.07613	13.13	0.8704

TABLE XXI.—EEL (*Anguilla rostrata*).

30°.....	0.4017	0.4012	0.4015	2.491	0.9135
50°.....	0.2026	0.2026	0.2026	4.938	0.9012
70°.....	0.1188	0.1185	0.1187	8.425	0.8880
90°.....	0.07800	0.07805	0.07803	12.81	0.8750

The viscosity measurements were made at practically the same time as when the other constants were determined, since the viscosity changes slowly, due to the decomposition of the oils. The following determinations of the viscosity of sperm oil taken two weeks after those, the results of which are given in Table VIII, show this, the later values being larger.

TABLE XXII.—VISCOSITY OF SPERM OIL.

Temp.	R. L.	L. L.	Av.
30°.....	0.3417	0.3424	0.3421
50°.....	0.1751	0.1754	0.1753
70°.....	0.1032	0.1029	0.1031
90°.....	0.06667	0.06661	0.06664

The question also arises whether the oils do not change in composition in being heated from 30°–90°, in such a way as to affect their viscosity, thereby introducing a complication into the study of the viscosity curves. That this is not the case may be seen from the following values for the viscosity of butterfish oil taken at 30° after measurements had been made on the same sample of oil from 30° up to 90°.

L. L.	R. L.	Av.
0.4282	0.4285	0.4284

The average value before heating was 0.4266, and the difference is therefore very small.

In one instance, that is with the sand shark oil, on standing for several weeks the oil became cloudy and there was deposited some solid fat. This was filtered from the liquid fats and measurements were taken again with the following results:

TABLE XXIII.—VISCOSITY OF SAND SHARK LIVER OIL (AFTER FILTRATION FROM SEPARATED SOLIDS).

Temp.	L. L.	R. L	Av.
30°.....	0.3703	0.3693	0.3698
50°.....	0.1942	0.1950	0.1946
70°.....	0.1179	0.1184	0.1182
90°.....	0.07990	0.07981	0.07986

The viscosity is in surprising agreement with that before the separation of the solid fats and about a half a per cent. higher.

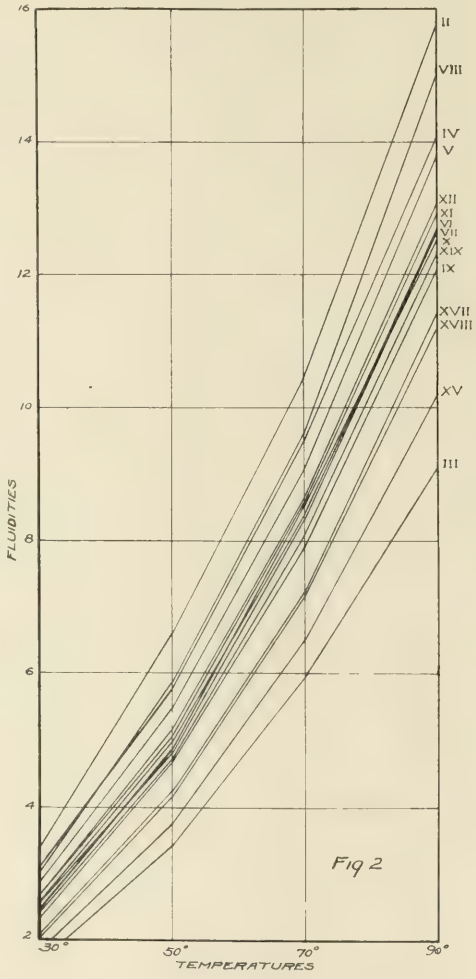
The influence of the degree of refinement of the oil on its viscosity is shown by the values for the two cod oils. Here again it is clear that the viscosimeter used is capable of making small differences in viscosity evident.

That the method for the extraction of the oils from the fish gave oils of characteristic viscosity is evidenced by the closely agreeing values for the various dogfish liver oils, which were obtained from different fish and extracted in the autoclave at different times. These oils were all a very light brown and no solids separated from them on standing. They also show close agreement in the values for the saponification number and the acid number. This is true of the two samples of torpedo oil although the viscosities do not agree so well. This latter fact is very probably due to physiological variances of an exceptional character, since one liver yielded apparently an abnormally large quantity of oil, while the other gave much less. Menhaden oils I and III approximated each other in color and in viscosity, whereas Menhaden II had a viscosity that was very high. This is explained by the fact that the last oil was extracted at a much higher temperature (130°) than the other two, whereby there was considerable decomposition and the oil became quite gummy.

The liver oils from the different members of the same family may be compared. In the shark family, the viscosities of the smooth dogfish, the spiny dogfish, and the sand shark liver oils are in the same order of magnitude, while that of the hammer-head shark is much higher than any of these. The values for the commercial whale and sperm oils, presumably refined according to similar methods, are very close to each other. A further study will be made of this problem.

No relation between the viscosity and the iodine number is apparent, as has been suggested by some investigators.

The results of the viscosity measurements were plotted and are shown in Fig. 2, the ordinates representing fluidities and the abscissas temperatures. The curve for each oil is numbered according to the table in which the viscosity values were presented. The graphs show that the fluidity of the different oils varies with the temperature in approximately the same way, and not linearly, the increase in fluidity being proportionally greater at the higher temperatures. The fluidities, and not the viscosities, were taken into consideration in view of Bingham's theories on the relations between fluidity and composition.[1] He believes, and has supported his belief with experimental data, that pure homogeneous liquids, which are not associated, have a fluidity which is a linear function of the temperature, the corresponding viscosity curve being hyperbolic. With liquids which are associated the fluidity curve deviates from a straight line to a degree dependent on the association. Assuming then that there is no chemical change in heating the oils from 30–90°, which was essentially proved in the case of the butter-fish oil, there is good evidence for the belief that these oils are more or less



associated at ordinary temperatures and that this association is broken down with rise in temperature. These oils are esters, and this theory is supported by the fact that esters are known to be associated. Viscosity measurements probably afford the best method for making this association evident.

The fluidity of oil mixtures will be discussed in a future paper.

SUMMARY.

1. A viscosimeter was devised capable of measuring

[1] *Z. physik. Chem.*, **66**, 1 (1909).

[1] *Ibid.*

the viscosity of oils with an accuracy which is very great. The viscosity of about twenty fish oils was measured at 30°, 50°, 70°, and 90°.

2. Measurements of the viscosity of these oils were taken at 30°. They were heated to 90°, cooled to 30°, and the viscosity redetermined, and it was found to be unaffected by the heating. The separation of solid fats from the sand shark liver oil causes little change in its viscosity, perhaps because the viscosity of these fats is practically identical with that of the oil.

3. The fluidities of the oils are not linear functions of the temperature, indicating that there is some association at the lower temperature. This theory is supported by the fact that esters have been shown to be associated.

The author wishes to express his gratitude to Mr. Adrian Thomas and Mr. William Crozier for aid during the course of this investigation.

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LABORATORY AND PLANT

HARDNESS OF PLASTERS AND CEMENTS, AND A SIMPLE CHRONOGRAPHIC APPARATUS FOR RECORDING SET.[1]

By CHAS. F. MCKENNA.

Received Jan. 10, 1912.

One cannot give a clear definition of the term "hardness" which will serve for all the meanings in which it is used. The mineralogist using Moh's Scale always means by this a measure of resistance to scratching or abrading; the wood-worker means the resistance to cutting; the steel-maker sometimes means by it the resistance to deformation under applied loads; in fact, indentation tests rule in many fields rather than scratching, cutting, or any other form of test.

In the case of hydraulic cements, the first stages of hardening have been usually measured by resistance to penetration; the later stages by finding the increase of cohesion determined by resistance on uniform cross-section to tractive or compressive forces gradually applied until rupture occurs.

The *setting* of plasters and cements is the very first stiffening and rapid development of cohesion up to the stage where needle points under moderate pressures do not penetrate the surface, or where small test objects are easily handled without fracture. Beyond this the phenomenon in which the cohesion due to complex mineral-forming reactions is step by step increased until a considerable age is reached is called the *hardening*.

The chemical phenomena occurring in the setting of plaster of Paris are chiefly those due to the energy in supersaturated solutions. Where a small proportion of water is used a hydrated sulphate of lime of one form goes into solution and the concentration causes the settling out or solidification of another form of hydrated sulphate; the water released from this helps to dissolve more again of the first form, which, by concentration, duly deposits again, and thus the process is continuous to total solidification. Similar phenomena can be observed in super-saturated solutions of some salts, which can be caused to deposit crystals and thicken almost to total solidification. The setting of such a compound of hydrated sulphate of lime is rapid, and except for effects of drying, the maximum hardness is obtained a very few hours after the gauging.

[1] Paper presented at the Fourth Annual Meeting, American Institute of Chemical Engineers, Washington, December 20, 1911.

In the setting of hydraulic cements we have something much more complex, though we have been instructed by the case of plaster and by some of the points of similarity in it.

Powdered Portland cement clinker is a complex solid solution of silicates and aluminates high in lime. When it is wet the alkaline lime solution resulting reacts on the silicates, producing a colloidal mass. A thermal effect occurring here in the beginning is the absorption of heat due to solution or the passage of the solid salts into the ionic condition.

In the setting of cement the first gelatinous mass formed is less and less permeable, due to drawing away of water coincident with the lowering of temperature; then as the crystal formation begins, the proportion of free water momentarily increases again and softens the colloids. Later, the full interlacing of crystals and the drying of the colloid admit less and less of penetration, and thus we have the development and finally the end of the process of setting.

Hardening can then go on through further molecular interchanges leading up to the formation of silicates of lime and alumina analogous to some of the hydrous silicates of mineralogy.

According to Michaelis, the exact steps are described as practically a migration of water throughout the mass. The first particles of clinker are dissolved on the surface; the supersaturated lime solution thus formed reacts to form a gelatinous mass, and when crystals of aluminate of lime are formed the water separated goes further to attack newer particles of the clinker nodule, later deserting the colloids formed and passing into the air or into the water in which it is immersed.

These reactions are complicated again by the presence of sulphate of lime, which serves to form with the aluminates of lime a double compound of slow-setting qualities, neutralizing the usual effect in a cement rich in aluminates of lime, where the setting is very quick and the development of heat sudden and great. Thus you will observe we consider setting to be consequential upon the formation of both colloids and crystalloids.

Apparatus for observing these changes in the setting process have usually been simple. For expert-

workers it suffices to use the thumb-nail. With skill and accustomed observation they thus obtain a definition which is as remarkable as the means are simple. Nothing has been developed towards providing means for observing set in plaster of Paris; the contraction and dilation, however, have been observed by van't Hoff in a beautifully simple apparatus.[1]

General Gilmore recommended, for observing set in Portland cement, a weighted coarse wire and a more heavily weighted fine wire (Fig. 1) for the determination, respectively, of the first stiffening (initial set), and the firm resistance to any penetra-

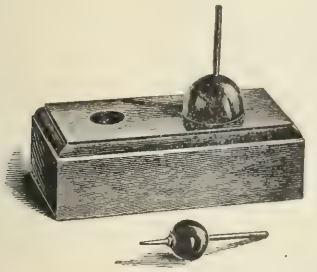


Fig 1.

tion or deformation (final set). Neither of these methods are instrumental or fitted to record distinct differences.

The first apparatus designed for such a purpose was that of Vicat, the French chemist and authority on cements. The Vicat needle (Fig. 2) is a weighted one, cylindrical and 1 square millimeter in area on the face, moving in a vertical scaled-off guide and falling upon the mass of gauged cement in a mold

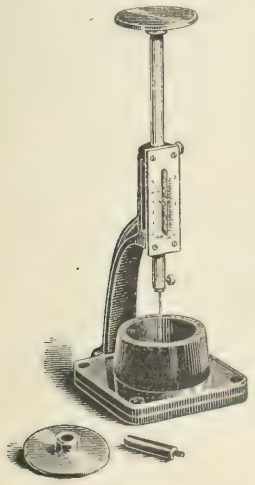


Fig 2

below. The initial set is taken as the time at which the needle will not penetrate within a certain distance of the bottom of the mass, and final set as the time when there will be no mark upon the surface from the needle.

However, chronographic and automatic apparatus have been sought for.

Professor A. Martens, of Charlottenburg, designed an apparatus in which needles energized by magnets are dropped and raised again as a clock movement makes the contacts.

The Amsler-Laffon cement setting recorder (Fig. 3) has been used in Europe. This is described in the journal "*Cement*," from which the accompanying figure is taken, and the following description: In testing the activity of cements by this apparatus two molds are filled with a plastic paste and two needles are lowered upon the cement at certain intervals, penetrating more or less into the mortar according to the progress of setting. The depth to which each needle enters the mortars is recorded on a drum by two separate pencils. After each strike of the needles the drum turns a little and the table on which the molds rest advances a step from right to left. The needle-holders are lowered and raised by a lever, which is set in motion by a spiral spring; a clock movement lets loose a governor and stops it again when the strike of the lever is completed. The diameter of the needles is one millimeter. The weight of each needle-holder is 300 grams.

The Nicol Spissograph (Fig. 4), the invention of R. Gordon Nicol, of Aberdeen, Scotland, and made by A. and J. Smith, of that city, is similarly designed. This apparatus consists of a clockwork which raises and lowers, every three minutes, a pointed needle; at the same time the paste is rotated in a spiral to present a different spot to the needle at every contact. On the apparatus is a thermograph recording on the same chart the temperature of the air at the time the test is made. The whole is covered with a glass case, and arrangements are made for keeping the temperature and humidity regular.

One of the best achievements in this line has been Gary's apparatus and the resulting investigations. He used the thermal changes during setting as the basis of study, and by photographing the changes of the mercury columns secured data for a chart (Fig. 5). Such a record as was thus secured gives admirable indications of the energy at work. None of these automatic instruments has been used in this country as far as I know.

The following is an extract from the official report of R. Feret, Boulogne-sur-Mer, at the Fifth Congress of the International Society for Testing Materials, held at Copenhagen in 1909:

"DURATION OF SETTING."

"The use of the Vicat needle continues to be the only practical method in use for the determination of the duration of the period of setting of hydraulic cements. The appliance is of extreme simplicity, but its readings are sometimes uncertain, especially when it is a question of determining the end of the period; besides, the readings are of a purely con-

[1] *Z. phys. Chem.*, **70**, 146.

ventional character and do not appear always to bear a sufficiently constant relation to the duration of the setting period of the mortars of actual practice. The discovery of more exact methods has therefore been attempted. Methods of testing based on the measured variations in the electric resistance of mortars while hardening have not given results of interest.

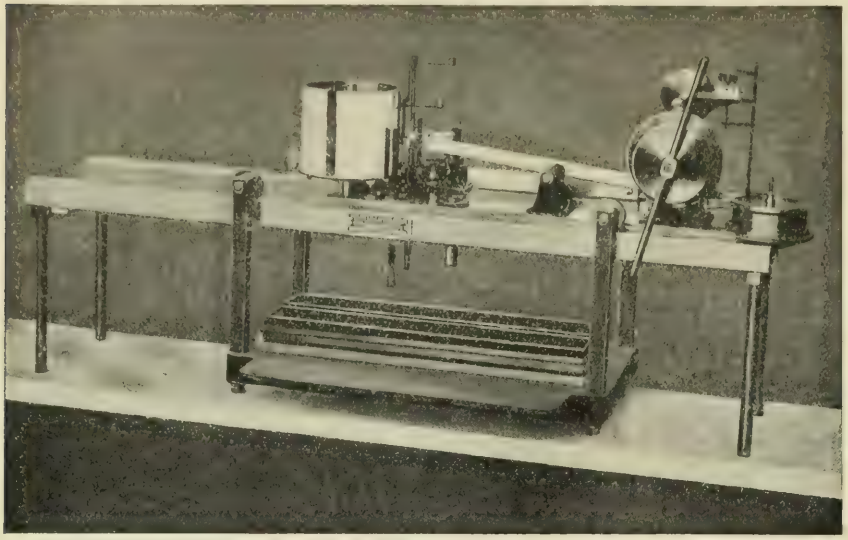


Fig. 3.

"Other investigations have aimed at the definition of the setting by the determination of the temperature of the mortar during its continuance. Reasonably regular curves were obtained by this method, which, however, were dependent on the testing conditions and corresponded with chemical phenomena, the relation of which to the change of consistency called setting has not yet been quite clearly established.

"The principal nature of the method to be employed may be the ascertainment of the time, reckoned from the commencement of the gauging, during which a given mortar can, with impunity, be further used without having to be revived by a fresh addition of water or a too violent mechanical treatment."

Reading this I was led to take up again certain studies of setting which I had made some years before, in which I was observing the resistance to penetration by glass rods, and the resistance to withdrawal of glass threads progressively acted upon by the salts and compounds formed in the paste and operating during the setting process. I thought that the holding power of newly formed salts upon glass might be progressively observed. Also it seemed to me then that the testing of the surface by wire points showed a lack of effectiveness in determining set in colloids and crystallo-colloidal binding agents. Penetration along a plane similar to shear by a knife blade should give better results than mere resistance to rupture of a surface at one point, just as the cutting of metal by a turning tool affords a better test of cohesion than indentation or scratching does.

If several glass rods or pins, ten or fifteen-thousandths of an inch in diameter, are driven into soft paste of plaster or cement, and at intervals are tipped forward, they will cut the mass at first considerably; later to a diminishing extent; and finally when the colloids and crystals are both well formed about the pins (a period corresponding with the final set or resistance to the light wire heavily loaded) they snap off sharply and suddenly. Such a combination seemed to give indications of very fine and measurable differences.

Now if you were to bring up against a line of such

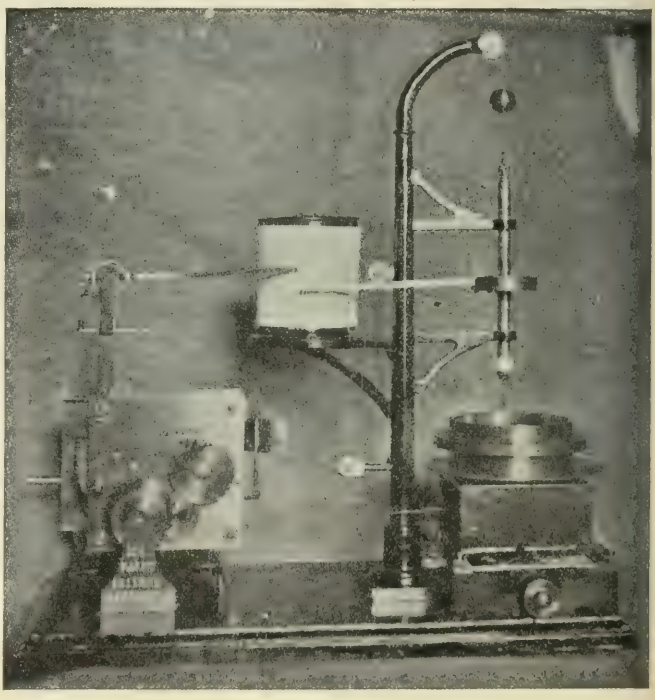


Fig. 4

pins a glass rod which had been smoked, you ought to get markings on it making a record showing relatively the resistances to penetration.

It seemed to me that this afforded a means of operating a graphic and chronological method, and

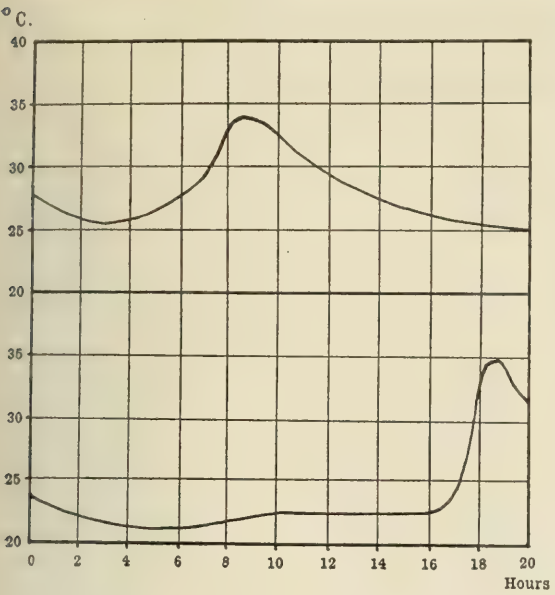


Fig. 5.

I have made many models of apparatus for such a purpose by making simple adaptations of things at hand till the present model was developed and put lately into this final form by Messrs. Schneider Bros., of Jersey City, the gifted mechanicians who are known all over the world for the simplicity and beauty of their work on scientific instruments.

I will explain in as few words as I can the operation of this instrument (Fig. 6). It consists of a screw, H, operated by clockwork, giving two speeds, there being a shifting lever, L, for a speed of one inch an hour and another speed of double that. It can also be operated by hand through a knurled head at one end. This screw, H, carries a moving finger, F, projecting over a long rectangular paste mould, C. This moves forward and strikes successively the glass pins P inserted deeply into the paste and projecting vertically from it in one line. As each glass pin bends forward it bears against a smoked glass rod and traces its path until, when a distinct resistance is attained, it snaps off. Back of this is an adjusting frame to carry the glass rod, and this can be brought forward very delicately, or drawn back, by the aid of a fine adjusting screw, A, at the back. A metal mold is filled with freshly gauged cement and run into place between the screw and the adjusting frame. The glass rod, which has been previously smoked and then rubbed clean over one-half of its surface, is inserted in the frame and brought forward over the center of the paste so that against the clean part of its surface these little pins are guided by it as they are inserted. So far as my investigations have gone I find that fifteen one-thousandths of an inch (0.015) give strength enough for meeting resistance and at the same time giving a tendency to snap. They are pushed in vertically along the middle line one-half inch apart; the glass rod is drawn back by the screw A and the untouched smoked part is turned over so that it can be brought up against the pins by the screw again, ready for any record. Then the clock is started, the finger begins to move, and as it strikes each pin successively it makes the respective record of the resistance to penetration at that point and time. A maximum and minimum thermometer can be attached to the base plate.

When everything is thus arranged the top glass case, can be put over it, leaving a small dish of water in the case, and the whole may be left for instance over night. In the morning the entire record is on the glass rod. Records thus made resemble the markings in Fig. 7.

(The record given for plaster of Paris is not symmetrical as to time, as the legend shows.)

These glass rods, with the records upon them, can be varnished and preserved for examination at any time, or the record can be photographed on sensitive paper and thus preserved.

From plaster of Paris I obtained a simple record of differences in resistance to penetration. I have not had many opportunities to experiment with varieties of this substance, but I expect to find that the instrument will readily indicate the differences due to changes in percentages of water, catalytic agents, etc.

From Portland cement the first few records already obtained are most interesting. It seems that in every normal Portland cement I have thus tested

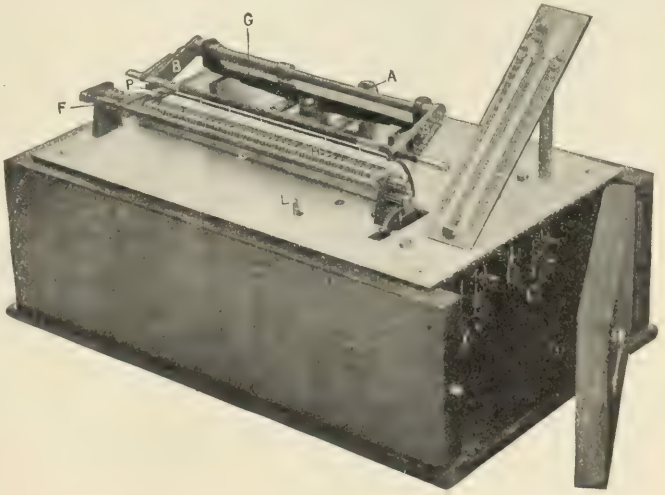


Fig. 6.

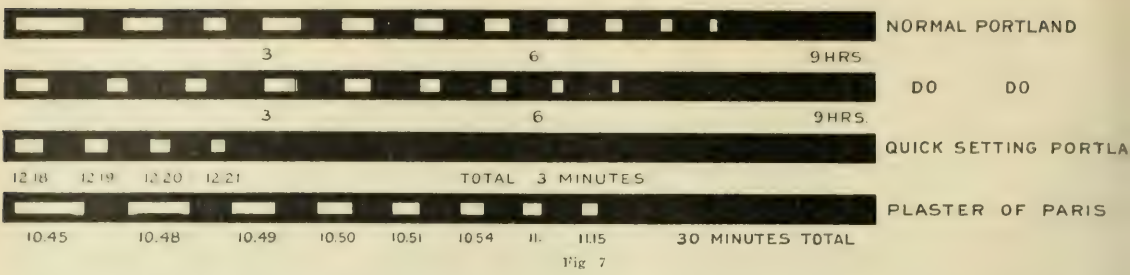


Fig 7

there is observable in or about the third hour an indication of a relaxation of the stiffness first obtained and then a resumption of hardening. Comparing these results with those of Gary's thermal studies, it is seen that he observed a marked lowering of temperature at or about the third hour. If we consider again the most modern theories of setting, I think we can explain this. The cooling effect of course is at the period when salts are going into solution most rapidly.

It is well known that if a break occurs in a temperature-solubility curve which is otherwise continuous, it is a proof that the solid substance which is in equilibrium with the solution, has passed into another form at the temperature of the break. We have the reverse of this in our record of cohesion, namely, that the break in continuity of the marks of increasing cohesion indicates the separating out from a saturated solution of a greater proportion of still another component, and that the water thus freed permeates the colloid and softens it. Later by desiccation, by absorption of the water within and further crystallization, cohesion begins to increase and impenetrability and hardness go on. The discovery of this slack period or reverse set explains contradictions experienced in the past in measuring or determining the initial set by the surface penetration system. It probably also will explain anomalies occurring in the practical use of cement during the first hours of gauging fresh cement.

If this observation of change in the order of setting should prove to be universal for cements with the sulphate of lime additament, we may have to observe first *initial set*, then *reverse set*, and lastly *final set*, and distinguish between them in time and character.

It is my intention to continue work as opportunity presents on this instrument, which appears to be simple and useful, and in time we may hope to reach a little further in our knowledge of the setting of plasters and cements.

LABORATORY OF CHAS. F. MCKENNA,
NEW YORK, December, 1911.

RECENT IMPROVEMENTS IN FILTRATION METHODS.[1]

By ERNST J. SWEETLAND.

Received Jan. 6, 1912.

Probably the simplest method of filtration is that of pouring the liquid to be filtered into a suspended bag and catching the solid matter in the bag while the filtrate is caught in a receptacle below. This method was conceived in the kitchen and has been used by house-wives for generations. Although it seems primitive, it is the method at present employed in most cane-sugar refineries. The great disadvantage of bag-filtration is that the bags have to be turned inside out to be cleaned.

The method of filtering through bags inwardly, that is, passing the liquid from the outside of the bag and draining the filtrate from the interior, has also been employed in sugar-house work to a limited extent. By this method the solids are deposited on the outside of the bag, and it is, therefore, more easily cleaned. In this type the usual arrangement is to enclose a corrugated plate or grid in the flattened bag to prevent it collapsing under external pressure, and a series of bags so arranged is enclosed in a box capable of sustaining a moderate pressure.

A flat filter-bag provided with means to prevent it from collapsing when subjected to external pressure, and having a suitable drainage outlet for filtered liquor, constitutes a filter-leaf. The different methods by which filter-leaves may be constructed are too numerous to be described in detail here.

The first large leaf-filter installations were introduced in the cyanide process, and were of the vacuum type.

In the vacuum leaf-filter the leaves are arranged in groups and submerged in the liquid to be filtered, and suction applied to the interior of the leaves. The partial vacuum formed draws the filtrate into the leaves, whence it drains to the vacuum receiver, or in the absence of a receiver it is drawn directly through the vacuum pump.

Vacuum leaf-filters are divided into two classes, namely, the movable leaf type and the stationary leaf type. In the former (Fig. 1) the "cake" of residue is first deposited on the surface of the leaf

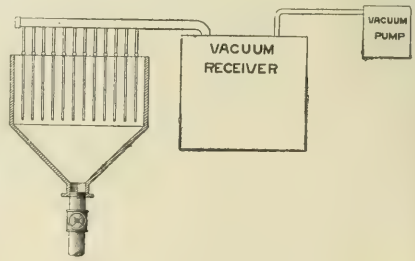


Fig. 1.

[1] Presented at the meeting of the American Chemical Society, New York, January 5, 1912.

to a thickness of one-half to three-quarters of an inch. The sludge[1] is then withdrawn from the filter-box, and wash water is admitted to take its place. During the time the change from sludge to wash water is taking place vacuum is maintained in the leaves to prevent the cakes from dropping off. The cakes will not fall as long as the vacuum is continued. As soon as the leaves are submerged in the wash water, washing commences, and is continued until the valuable solution in the cake has been displaced with water. When this is done the suction is discontinued.

The next step is to dislodge the cakes from the filter-leaves and discharge them. This is done by simply admitting compressed air into the leaves, which bulges the cloth slightly and the cakes immediately fall to the bottom of the hopper.

When the cakes have fallen the surplus water in the box is decanted off for re-use, and the pasty mass of cake is discharged through a large valve at the bottom of the hopper.

The operation of the movable leaf type is similar to that of the stationary type, except that instead of the sludge and wash water being transferred, the group of leaves is transferred by a traveling crane from a sludge tank to a wash-water tank.

The requirements of a filter in the cyanide process are most exacting. When it is noted that a moderate sized plant will handle three or four hundred tons of ore residue, or slime, per 24 hours; that the cost of filtering must be well under ten cents per ton of dry ore filtered; that the element in solution to be recovered by washing is in many cases gold, worth $20 67 per ounce, the importance of the filter is realized.

In the case of a cyanide filter working on a gold ore, in good practice the amount of dissolved gold which escapes recovery will range from one two-hundredth to one five-hundredth of an ounce per ton of dry residue, or say about one grain per ton.

This splendid washing efficiency is due to what I shall take the liberty of calling "direct contact washing." The cake is deposited in an even layer on the leaf and, when submerged, is in direct contact with the wash water. The cake has been deposited in a natural unrestricted manner without packing or crowding, and with an even pressure in all directions. A cake deposited in this manner, will, if all conditions are suited to the material in hand, be of even thickness throughout and of even density, but if during the cake-forming, some disturbing influence enters, which tends to cause the cake to vary in thickness, the density, or perviousness of the cake will automatically adjust itself to suit the varying conditions, which insures even washing.

The rate of percolation through the cake is governed by the resistance offered by the cake and the pressure of the liquid against the cake.

Other conditions being equal, two cakes of the same thickness, and of the same degree of porosity, will offer equal resistance to percolation, and therefore filter at equal rates per unit of area.

[1] The term "sludge" as here used refers to a fluid mixture of liquid and solid matter to be filtered.

If two cakes vary in resistance they must vary in thickness in order to be equally washed in a given time.

To properly consider these statements it is necessary to consider the resistance of the filter-cloth as well as that of the cake; that is, the resistance per square foot of cake is equal to the resistance of one square foot of cake plus the resistance of the square foot of cloth underlying it.

For example, suppose that for some reason a portion of the cloth of a filter-leaf has become partially obstructed and offers more resistance than the rest of the leaf. While cake-forming is in progress the cake formed on this partially obstructed spot will be thinner than that in other places. Now when the cake is submerged in wash water the resistance which limited the thickness of the cake in this spot again comes into play, and limits the amount of wash water which passes through it. In this manner the thin cake receives an amount of wash water proportionate in its volume.

Before proceeding let us compare the cake-forming and washing in a common plate and frame filter press with the same in leaf-filters. In forming a filter cake with any material there is a certain point where the rate of filtration begins to drop off very rapidly, due to the resistance offered by the cake. When this decrease has been noted, the cake has reached the economical limit of thickness, and to proceed farther is a waste of time and power. For instance, it has been noted that with certain colloidal materials a cake of one-half inch can be formed in about thirty minutes, but at this point filtration becomes so slow that to increase this cake to one inch in thickness would take several hours. Obviously this would not be economical.

In a plate and frame press each wall of the frame cell is a filtering wall, and the cake builds up on each wall until the two adjacent cakes finally join together to form a single cake filling the entire cell. In Fig. 2,

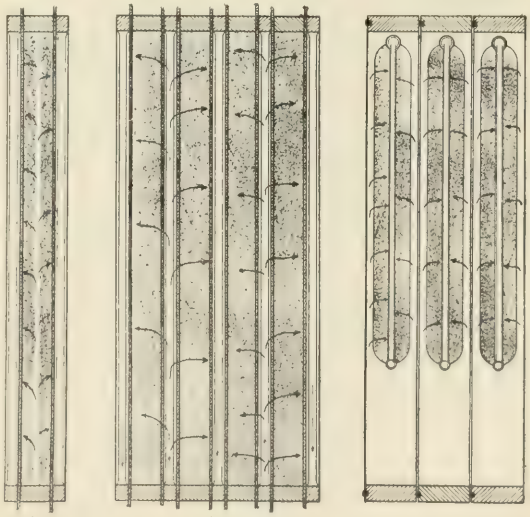


Fig. 2

a shows the cake partly formed, and the arrows indicate flow in both directions while filling the press. In *b* the cells are shown filled, the arrows indicating direction of flow of wash water; *c* shows cakes on filter-leaves and the arrows indicate the direction of flow both while cake-forming and washing.

Now to get the maximum cake-forming capacity from the filter press, the cake formed on each cloth must be up to the economical limit of thickness. This is all right if washing is not contemplated, but if the cake is to be washed we find that wash water has to be forced through a cake twice as thick as it should be.

If to overcome this objection the thickness of the frame be reduced to give a cake of proper thickness for washing, then the capacity of the filter press for cake-forming is greatly reduced. In all cases the frame must be solidly filled with cake, as otherwise the line of junction between the cakes formed on opposite surfaces of the cell will be soft and make good washing impossible. Furthermore, if the solid matter in hand varies in structure, some of it being granular while the rest is colloidal, the granular particles will tend to settle to the bottom of the filter press frames, making the lower portion of the cake more porous than the upper portion, and when washing is in progress the bulk of the wash water passes through the lower portion of the cake, leaving the upper part imperfectly washed.

Again, some cakes tend to shrink during washing, and shrink away from the rigid walls of the frames, leaving channels through which a portion of the wash water passes, unduly increasing the volume of wash water, and impairing the efficiency of the wash.

In leaf-filters the maximum economical thickness of cake can be formed, because the cake is washed exactly as it is formed; a double thickness of cake never has to be washed. Then, too, in the leaf-filter, the direction of flow during washing is the same as during cake-forming, while in the plate and frame press one-half of the cake is washed in the opposite direction to which it was formed against the grain, and this tends to disturb the natural arrangement of the particles.

If the texture of the cake-forming material in which a filter-leaf is operating varies, and the granular portion settles toward the bottom, the thickness of the cake will vary, and be thicker at the bottom than at the top, so that the granular portion which admits of the more rapid passage of wash water, is thicker than the less porous portion, and really *requires* more washing.

What are technically known as vacuum filters are, in reality, pressure filters, operated by atmospheric pressure. Obviously in an open filter of this type the maximum pressure that can be brought to bear under ideal conditions would be 14.7 lbs. per square inch. Under practical conditions the vacuum maintained is usually about 22″ or the equivalent of 11 pounds pressure per square inch. Since the rate of filtration is in proportion to the pressure, the low pressure available in vacuum filtration makes the size of installation necessary for a given capacity very large. This gives rise to a number of objections, namely:

Large initial cost.

Large floor space and head room required.

Excessive power consumption.

High cost of maintenance.

In addition to these, vacuum filters are entirely unavailable for filtering hot solutions.

The logical means of overcoming the objections cited is to enclose the filter-leaves in a chamber so that greater pressure can be used and thus greatly reduce the size of the installation, since the principles governing leaf-filtration apply regardless of whether suction or external pressure is used.

The difference between vacuum and pressure filters has been aptly explained by saying that in the former the liquid is pulled through the cloth while in the latter it is pushed through.

The number of mechanical arrangements by which pressure leaf-filters may be constructed are many. Of these, three different types have been in operation on a large scale for some time. These are the Kelly, the Burt and the Sweetland filters.

The Kelly filter comprises a plurality of leaves mounted on the door of a steel shell and provided with rollers by means of which the groups of leaves may be rolled into the steel shell and the door bolted in place. When ready for discharge the door is unfastened and the leaves rolled out of the shell.

The Burt filter comprises an inclined steel shell with vertical leaves suspended at intervals throughout the length of the shell. The cakes are discharged through a door on the lower end of the shell.

In designing the Sweetland filter I endeavored to keep in view the great importance of easy accessibility of all the parts for examination or renewal, and at the same time provide a construction of such flexibility as to meet the many and varied demands of the chemical and metallurgical industries. In general appearance the Sweetland filter somewhat resembles the standard type of plate and frame filter press, that is, it comprises a series of frames resting upon a pair of side bars, and an end piece, or head, forms a closure for each end. Each frame carries an inserted gasket of rubber or other suitable material, and the frames are clamped together to form a water-tight chamber by means of a heavy screw bearing against the movable head (Figs. 3 and 4).

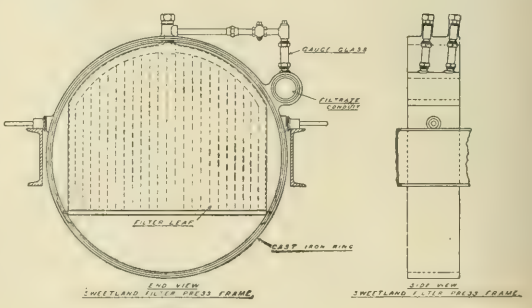


Fig. 3.

Each frame carries a removable leaf, and in this usual construction a space is left between the bottom of the leaf and the lower wall of the frame.

The operation is as follows: the liquid to be filtered is admitted to the chamber through an inlet at the bottom; while filling the enclosed air-escapes through a valve at the top. When the air-escape valve is closed the pressure increases within the chamber and filtration begins. When the cake has formed to a suitable thickness the source of supply is shut off and the excess unfiltered liquid is withdrawn from the chamber.

In most cases the cake will adhere to the leaf without assistance, but in case the material in hand shows a tendency to drop off the leaves, the cakes are held in place by vacuum applied to the interior of the leaves. The excess having been removed, wash water is admitted to the chamber under pressure, the enclosed air being allowed to escape as before. The wash water percolates through the cakes and displaces the soluble salts. This done, the excess wash water is withdrawn for future use.

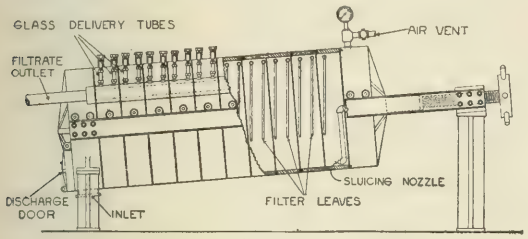


Fig. 4.

The cakes are now to be discharged. If wet discharging is permissible, water under pressure is turned through the discharge nozzles at the upper end of the press. The cakes are then forced off of the filter-leaves with compressed air, and as they fall to the bottom they are rapidly sluiced out through the discharge door in the lower head of the press.

If it is desired to remove the cakes as dry as possible they are then dropped into a tray which is inserted into the space in the bottom of the press, or else they are allowed to drop into the space below the leaves and are removed with a hoe or scraper.

If the Sweetland filter is used to clarify a solution containing but a small percentage of solids, the space in the bottom of the press offers a material advantage, for in this space accumulated solids may be stored without obstruction to the filter surface. When the press is in operation in this manner it is allowed to run until accumulated solids on the leaves begin to materially decrease the rate of flow. When this occurs a puff of compressed air is admitted to the interior of the leaves, and the rush of air through the pores of the cloth in the contrary direction to filtration, disengages the solids from the filter-cloth, and the thin cakes fall to the bottom of the press, to lay there until sufficient has accumulated to justify opening the discharge door and flushing out the press.

The sectional construction described permits of a great many modifications. Lead-lined presses of this type have been built for acid solutions, the sheet lead lining being joined by fusion to lead rings which are cast into the edges of the cast-iron frames (Fig. 5).

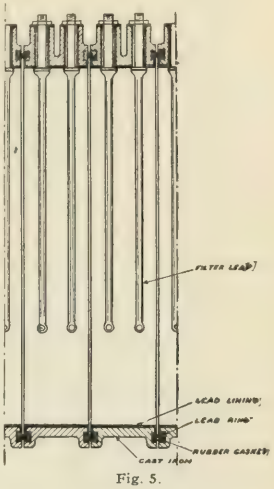


Fig. 5.

The frames are made of wood for such materials as make the use of metal impracticable, and in such presses the head pieces are made of cast iron with wooden linings, and a wooden tray may be used to receive the cakes when discharging (Fig. 6).

Bronze presses of the Sweetland type are built, and have particular advantage of being much lighter than plate and frame presses, since the filter-leaf takes the place of the heavy plate.

These presses have also been built with steam spaces in the frames for maintaining the heat of the liquor being filtered. These spaces do not in any way interfere with the sectional construction.

The possibilities of leaf-filtration are broadening every day. It has recently been demonstrated that in refining oils and fats with fuller's earth, the amount of oil left in the residue can be greatly reduced by the construction described.

The time is near at hand when bag-filters in cane-sugar refineries will be displaced by leaf-filters of the pressure type, for not only is cleaning of the

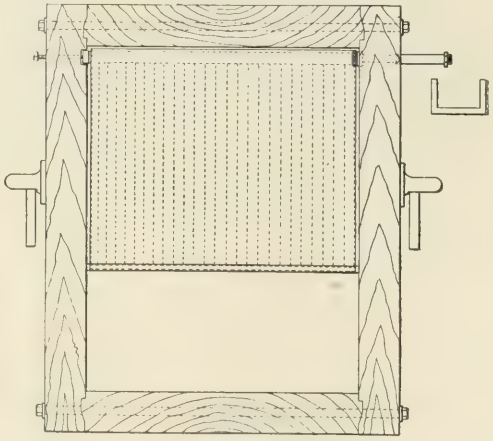


Fig. 6.

leaves made almost automatic by reversal of current through the cloth, coupled with suitable spraying devices, but the filter area required for a given capacity will be greatly reduced.

Experience has shown that filter-cloth made into leaves lasts longer than the same cloth used in plate and frame presses, because on the latter the cloth

is subject to handling, scraping, and other mechanical injury from being squeezed between the units of the filter press.

The filtering requirements of the chemical industry are so many and varied that it would be absurd to blindly advocate any specific construction as a cure for all filtering evils. Each problem must be approached with care and each installation properly designed to suit the needs of the material in hand, and when this is done higher efficiency and lower filtration costs will be realized.

AN ELECTRIC STILL ADAPTED FOR DIFFICULT DISTILLATIONS.[1]

By I. C. Allen and W. A. Jacobs.

GENERAL STATEMENT.

The process of separating two or more volatile liquids possessing different boiling points by distillation was one of the first processes employed in the early days of chemistry. With uncomplex mixtures it is comparatively simple. In early attempts at distillation the volatile substances were heated in earthen bottles over wood or charcoal fires; today they are heated in metal or glass retorts over gas flames.

The modern glass distilling flask heated with a Bunsen flame is too well known to need description here, but connected with its use are many difficulties that often are not fully appreciated. The continual wavering of the flame, even when it is most carefully screened from air currents, and the variations of the gas pressure subject the retort to uneven and intermittent heating. Such heating causes irregularity in the rate of distillation, and for this reason duplicate distillations do not yield distillates that are alike in quantity and quality. Also, strains in the glass are produced by this uneven heating, and the glass often cracks. With inflammable liquids this is a serious danger. With easily decomposable materials local superheating causes decomposition. Again, the upper parts of the flask are not directly heated, and these chill the vapors and cause them to drip back, thus retarding greatly the progress of the distillation.

In the distillation of petroleum, for instance, one has to do with a material composed of a great number of bodies or rather a number of series of bodies that range from the lightest petroleum ethers to solid paraffins and asphaltums and form a group, the adjacent members of which so closely resemble one another in their physical and chemical properties, that absolute differentiation is well-nigh impossible with the present methods of procedure. Close adjustment and control of temperature is the prime requisite in effecting the separation of these important series.

Dissatisfaction with the ordinary method of distillation led the authors to develop a still heated externally by electricity; this apparatus has given such satisfactory results that a description will be of value, it is believed, to those having to do with laboratory stills and similar heating devices.

DESCRIPTION OF STILL.

The Heater.

The heater here described was first furnished to the writers by Dr. David T. Day, of the United States Geological Survey, and has been used by him in the petroleum laboratory of the Survey at Washington, D. C. The pattern now used by the writers has been developed from his spherical pattern, and consists essentially of two pear-shaped halves of heat-resisting materials enclosing and closely fitting the retort or distilling flask. The halves hold on their inner or concave surfaces a metal resistance wire, wound back and forth (Fig. 2) for conducting an electric current. The electrically heated wire warms the flask and its contents, and boiling proceeds quietly, uniformly, and most satisfactorily.

Fig. 1 shows the still in its developed form as used in the petroleum laboratory of the Bureau of Mines.

Protection of Still Neck.

The heaters are wired, that is, the retorts are actually heated, throughout the entire length of the neck; they thus differ from the Day heaters, which are heated only to the base of the neck and have the neck jacketed. The retorts are heated throughout that there may be no cooling or dephlegmatory action in the still neck. If a naked neck is exposed to the variable air currents of the laboratory, chilling effects are bound to result; consequently, there will be variable condensation in the neck and resultant variations in the distillates.

The obtaining of uniform products in the distillation of petroleums depends not so much on rigid adherence to the exact dimensions of the retort[1] and the length and declination of the condenser, though these are important, as on maintaining absolute control of the heating itself. The condenser should be no longer than is necessary for a perfect cooling; a total length of 60 cm. should suffice.

With the lighter fractions of petroleums, such as naphthas and gasolines, or with mixtures of alcohols, ethers, or volatile substances in general, a fractionation with a proper dephlegmator gives a better separation than a fractionation without such a dephlegmator, particularly if a long evaporator neck[2] is used and is kept at a definite temperature by means of a water jacket or by means of an electrically heated jacket.

With the heavier oils, however, the continuous heating that is necessary when a dephlegmator is used causes a degradation in the quality of the distillates. In distilling such bodies as petroleums consisting of a solution of gasolines, kerosenes, lubri-

[1] Published from Bulletin 19, Bureau of Mines, by permission of the Director.

[1] Redwood, Boverton, "Engler's Fractionating System," "Petroleum and Its Products," Vol. II, pp 534–6 (1906). Holde, *Untersuchung der Mineralöle und Fette*, **1909**, pp. 20–2.

[2] Young, Sydney, "Fractional Distillations," **1903**, pp. 166–8.

cants, waxes, and solid asphaltums, a dephlegmator makes a clean cut separation of the naphthas, but delays the distillation of the kerosenes and absolutely prevents the fractionation of the heavier lubricants.

Therefore, to insure uniformity of results, to remove all oils that boil below their point of decomposition and to compare various oils under like methods of treatment, control of the temperature in the still and the still neck must be maintained in some manner.

The thermal influences of variable air currents on the still, particularly if it is not jacketed (the gas-heated retorts in most laboratories are usually without jackets), play an important rôle, but are in a measure overcome by incasing the entire retort with the heater.

Moreover, the lag of the distillates in the condenser, particularly noticeable in the case of heavier fractions, must be minimized by setting the cooler in a nearly vertical position and heating the cooling water as the distillates become viscous and move more sluggishly.

It is therefore considered advisable to maintain control of the thermal conditions in the retort and the still neck by warming the neck with the retort itself. Such warming is necessary with the heavier oils in order that the last portion of the vapors may be driven over and not be allowed to lag in the hot retort under conditions that cause superheating and consequent decomposition.

A simple jacketing of the still neck without special heating gives good results in the case of the lighter fractions—the naphthas and the lighter-burning oils—but does not suffice for the heavy lubricating fractions.

As there is little or no lag of the vapors in the still neck—this being of the same temperature throughout and the vapors being driven onward by the continuous and steady generation of more vapors from below—they can not be materially superheated while passing through the neck. Their clean odor, the absence of color, and the non-appearance of carbonaceous deposits at the base of the still neck, at least until the higher temperatures are reached, lead to this conclusion.

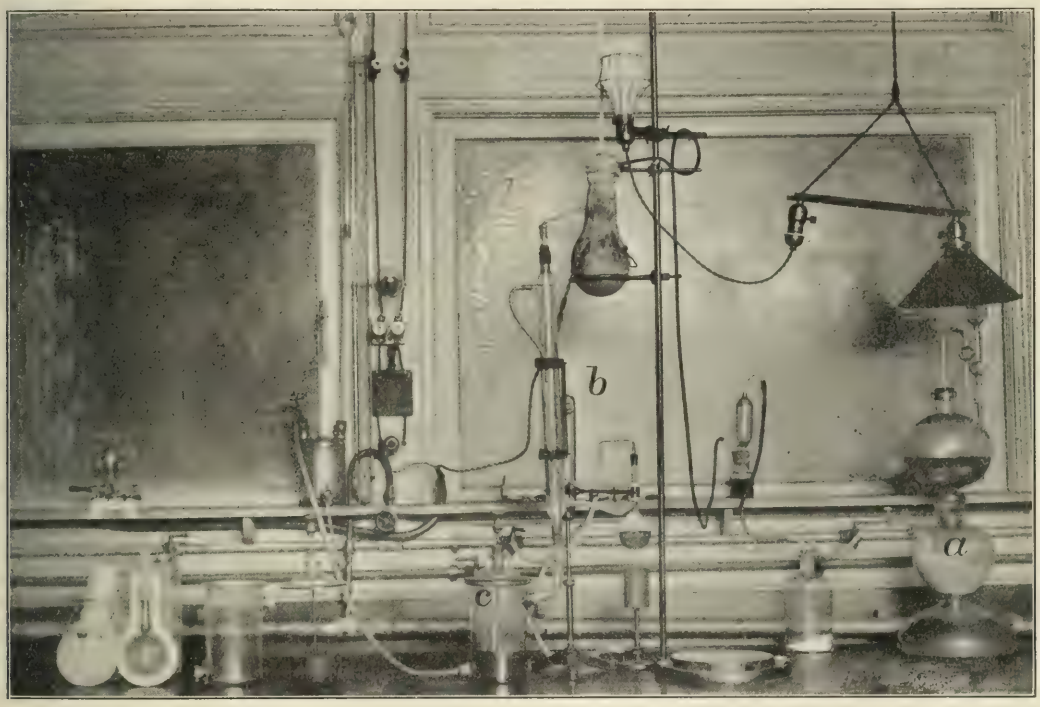


Fig. 1.—Petroleum still complete, showing CO_2 generator for driving out water vapors, electric heater, Liebig condenser with water heater, Bruehl receiver with receiving tubes, vacuum pump (Richards) with mercury manometer, electric connections leading to the left to the regulating rheostat (not shown in the cut). To the left is shown a dismantled heater and Bruehl receiver.

CONSTRUCTION OF THE STILL.

The Heater.

The body of the heater is composed of 100 parts by weight of powdered magnesia, 100 parts by weight of powdered silica, 40 parts by weight of finely shredded asbestos, and 10 parts by weight of powdered sodium silicate, thoroughly mixed together, dried, and made into a paste with a saturated aqueous solution of magnesium chloride. The use of this paste was suggested by Mr. A. V. Bleininger, formerly ceramics chemist of the United States Geological Survey. The paste may be molded into any form desired, and after setting over night it becomes hard and firm enough to endure gentle handling.

To prevent cracking and warping during the subsequent drying, the heater is warmed in an oven at about 50° C. for 48 hours, after which it is heated at 200° C. for several hours to expel the last traces of moisture. The heater is then hard and sufficiently strong for most laboratory purposes. It will endure heating, without corrosion of the wire and without injury to the insulating material, to the temperature at which the glass of the retort begins to soften, the highest temperature at which the heaters in the Pittsburgh laboratory have as yet been subjected.

This heater may be made in any desired form, for heating ovens, water baths, hot plates, viscosimeter jackets, etc., and is most admirably adapted for incasing a still neck or dephlegmator to maintain any desired temperature within, from room temperature up to the temperatures at which heavy oils decompose and carbonize.

Wiring the Heater.

The manner of wiring the heater for a distilling flask is most important. Wrapping the wires equidistant from one another from the bottom of the flask up to the top of the neck develops too great a heat in the neck and in consequence causes superheating of the heavier oil vapors.

Wrapping the wires from the bottom of the flask up to the base of the neck results in a dephlegmatory action in the neck that can not be controlled.

After repeated trials (shown graphically in Bull. 19, Bureau of Mines), the method of wiring shown has been developed. The method gives a nearly uniform temperature from the bottom of the boiling liquid to the side tube carrying off the vapors—a temperature which is always under the control of the operator.

Mold for Heater.

The forms for a distilling flask may conveniently be made as follows: Turn from a block of wood a model the size and form of the distilling flask, with the bulb and neck in one piece, and saw the model into halves from top to bottom. Hollow out the bulb and neck to form a shallow dipper, making the cavity about 1 cm. deep, and leaving the rim about 3 mm. thick. Drill holes the size of a small wire brad 1 cm. apart and 3 mm. below the edge of the rim of the dipper and along the handle or neck as far as it is desired to have the heating wire. Insert brads through these holes from the inside and allow the points to project about 3 mm., thus forming a comb of brad points around the outside of the dipper near the edge (Fig. 2(*a*)).

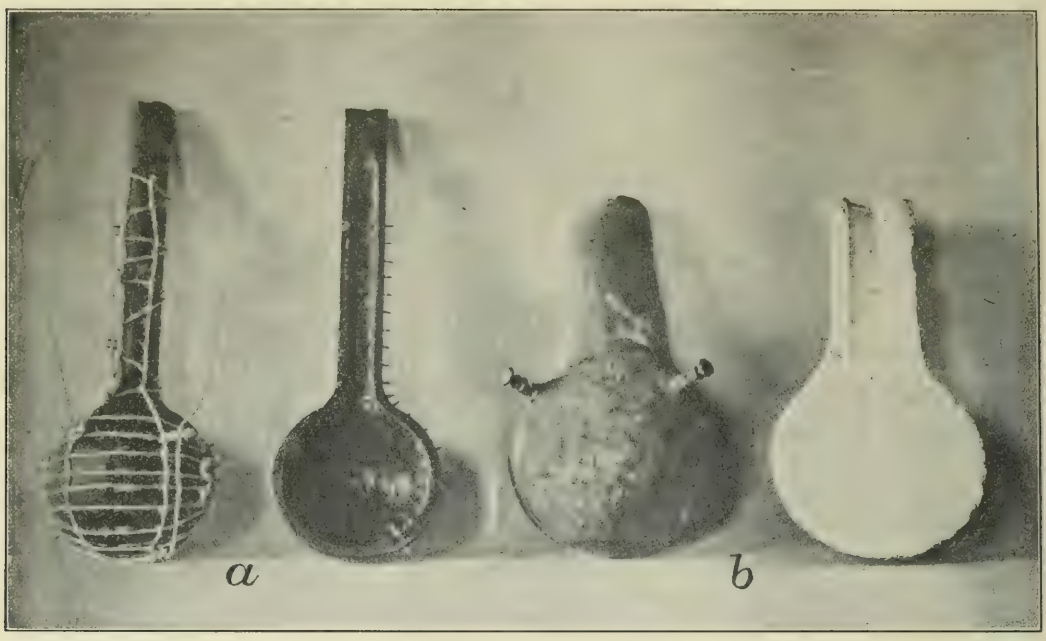


Fig. 2.—Electric heater and mold: (*a*) mold after and before wiring; (*b*) completed heater.

Then, after greasing well the convex surface of the mold to prevent the paste from sticking, wrap the heating wire back and forth, the wires being 1 cm. distant from one another, across the convex surface of the dipper between these points, in the manner shown in Fig. 2(*a*), tying the wire in place with asbestos cord and making its two ends fast to binding-post projecting at convenient positions. Lay the wired form, convex side up, on a smooth board covered with a sheet of paper and apply freshly prepared paste to the desired thickness, about 2 cm.

Allow the paste to harden over night. Remove the brads from the inside of the mold. The heater will then be released and ready for the final drying described above. Do not pass a current through the

wire until the heater has been thoroughly dried, else rapid corrosion of the wire will result.

A 1/8-liter heater requires about 500 grams of material and 3.5 meters of wire, a 1/4-liter heater about 1,000 grams of material and 5.5 meters of wire, and a 1-liter heater about 2,000 grams of material and 11 meters of wire.

The completed heater is shown at *b* in Fig. 2.

Wire.

Any high-resistance wire may be used. In the laboratory of the Bureau of Mines a No. 24 (B. & S.) nickel-chrome wire (the alloy contains about 60 per cent. nickel, 18 per cent. chromium, and 22 per cent. iron) insulated with asbestos is used. This wire has a resistance of about 0.00466 ohm per meter at 20° C.[1]

TEMPERATURE CONTROL.

The current, and therefore the temperature, are most admirably controlled by a simple water rheostat. Such a rheostat hardly needs a description as its principle is so well known. The one used consists simply of a 10-liter stone jar containing slightly saline water, a metal (preferably a carbon) plate at the bottom of the jar, and a triangular carbon plate that dips into the water and is suspended from a windlass. The plate at the bottom of the jar is connected with one side of the electric circuit in series with the heater, and the triangular plate is connected with the other side of the circuit (Fig. 3). By turning the windlass the upper plate may be lowered into the water and the current

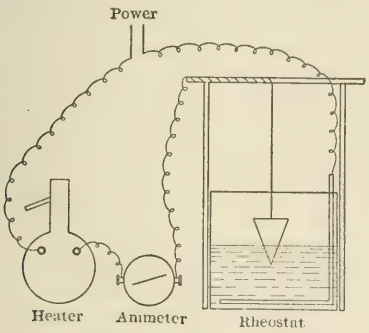


Fig. 3.—Arrangement of electric circuit for heater.

increased. The slightest turn, the lowering of the plate 1 mm. into the water, effects a change in the temperature of the heater. With a steady current, any temperature between the temperature of the room and the coking temperature of asphaltum is readily maintained throughout any reasonable time of distillation. Similarly, a digestion at any desired temperature may be carried on throughout a period of several hours.

Either alternating or direct current may be used, though the former is less destructive to the rheostat plates. In either case, however, the current must be carefully regulated by means of an ammeter during the entire distillation.

The current required ranges from a very low amperage, at the beginning of distillation, to 3 or 3.5 amperes at 220 volts, as the temperature approaches 325° C.

METHOD OF DISTILLING.

Position of Condenser—Use of Warming Oil.

The manner of petroleum distillation adopted in the Pittsburgh laboratory differs from the Engler method[1] in that the condenser is placed in a nearly vertical position instead of at the usual angle of 75° with the vertical. This is done in order that the distillates condensing in the cooler may flow into the receivers in the shortest possible time. Care must be exercised to prevent the direct falling of the drops to the lower end of the condenser, or the spattering will cause loss. When the condensed vapors flow quickly into the receivers, the reading of the thermometers at the outlet of the retort neck corresponds more nearly to the temperature of distillation of the distillate as collected in the receivers.

In order to reduce this time factor or lag in the condenser, a warming coil is arranged in the water system of the condenser (Fig. 1) whereby the water can be warmed as the distillates become more and more sluggish.

The distillation is continuous[2] and not intermittent[3] and is conducted as nearly as possible at the rate of 1 drop of distillate per second. This rate is continually controlled by observing the swing of a pendulum beating seconds, and carefully regulating the current according to this drip.

Arrangement of Receivers.

By arranging a Bruehl receiver with 10 or more receiving tubes, a fractionation of any ordinary petroleum may be carried on under atmospheric pressure up to the desired temperature, say 325° C., that is, nearly up to that temperature at which the petroleum begins to decompose, thus removing the naphthas and burning oils. Then, by simply replacing the receivers by empty ones (the temperature must be dropped to 125° C. in order to subject the oil to vacuum distillation), the distillation may be continued under a vacuum up to near the decomposing point of the petroleum residues, thereby removing the lubricating oils. The distillate cuts are made at each increment of 25° C. With an asphaltum oil this procedure gives 15 or 20 fractions and leaves a dry, brittle asphaltum residue without causing undue decomposition of the distillates or carbonization of the residue. It is to be noted that before the distillation of the lubricating oils under vacuum begins, the receivers containing the naphthas and burning oils should be removed, else a considerable percentage of these fractions will

[1] This wire may be obtained from the Driver-Harris Wire Co., Newark, N. J.

[1] Redwood, Boverton, "Petroleum and Its Products," Vol. II, pp. 534–536 (1906). Holde, *Untersuchung der Mineralöle und Fette*, **1909**, pp. 20–22.

[2] Ubbelohde, L., "Fixation de la limite d'ebullition du pétrole," *Moniteur du pétrole Roumain*, March 10, 1908, pp. 279–83.

[3] Redwood, Boverton, "Petroleum and Its Products," Vol. II, pp. 534–36 (1906). Holde, *Untersuchung der Mineralöle und Fette*, **1909**, pp. 20–22.

be volatilized and lost. Also in distilling light oils the receivers should be packed in ice to prevent volatilization of the lighter portions of the oils during the distillation.

Minor Details.

In order that a high vacuum may be maintained successfully, it is advisable to lute all joints with a thin paste of glycerin and litharge, which rapidly hardens and forms a strong air-tight seal. Very effective litharge, canary-yellow in color, is readily prepared by heating finely pulverized (200-mesh) commercial litharge or, better, chemically pure lead carbonate, in an electric furnace at 600° C. for 45 minutes.

Great care must be exercised in observing the barometric and the vacuum pressures during the distillations, the vacuum should be maintained as near a constant as possible, and corrections should be made for the boiling-point[1] if one would duplicate his work.

By making use of a good "evaporator neck" either ice cooled or electrically heated, according to the temperature desired, an elaborate refractionation of any desired distillate may be accomplished, and any petroleum may be readily separated not only into its technologic components, but also into bodies having fairly definite boiling points.

The rapid removal of the distillable oils from the asphaltum residue is thought to be advisable because the latter is of variable and unstable composition, and continuous heating degrades the quality of the distillates and injures the properties of the asphaltum itself.

All distillations are made by weight, the flask and receivers being weighed empty and with contents. This procedure is more convenient and more accurate than measuring by volume.

Accuracy of Distillations.

The heaters described are used either for the lightest gasolines or for semisolid bitumens. As an example of the readiness with which difficult distillations can be conducted with the above still, there has been distilled without difficulty an emulsified crude petroleum, an analysis of which gave the following results:

	Per cent.
Water	33.0
Distillable oils, atmospheric pressure	9.4
Distillable oils, vacuum pressure of 18 mm. mercury	25.8
Asphaltum, brittle at room temperatures	29.4
Sand, etc.	1.0
Total distillation losses	1.4
	100.0

Again, a petroleum fractionation made in duplicate by means of this still gave the following results:

Air fractions (747 mm. pressure):	I. Per cent.	II. Per cent.
175–200° C.	0.9	0.9
200–225° C.	14.5	14.1
225–250° C.	9.0	9.4
250–275° C.	7.6	7.5
275–300° C.	7.6	7.6
300–325° C.	8.2	8.1
Total	47.8	47.6

[1] Young, "Fractional Distillation," **1903**, pp. 14–16

Vacuum fractions (31 mm. pressure):	I. Per cent.	II. Per cent.
200–225° C.	2.9	3.0
225–250° C.	4.2	4.0
250–275° C.	4.3	4.6
275–300° C.	5.3	4.8
300–325° C.	6.3	7.0
Total	23.0	23.4
Residue	28.0	27.8
Distilling loss	1.2	1.2
Total residue and losses	29.2	29.0
	100.0	100.0

Prevention of "Bumping."

In the internally-heated apparatus described by Beckmann[1] in his account of his boiling-point determinations there is mention of "bumping" when he was boiling anilin (boiling point 184° C. at 760 mm.). In the above externally-heated still there is used in this laboratory, as in many other laboratories, a "boiling stone" of porous porcelain (or of a pumice stone for the lighter oils) weighing about 0.5 gram, and no trouble from bumping is experienced even with heavy oils that boil at temperatures as high as 325° C. under a vacuum of 20 mm. mercury pressure.

Richards and Matthews, in describing their internally heated still, remark:[2]

In brief, this note (description) shows that while distillation by means of a wire heated electrically effects a somewhat better separation than the ordinary method and causes much less superheating in the liquid, the gain in efficiency of separation is not always as great as had been at first inferred from the great constancy of boiling point observed in a special series of cases.

This result is to be expected, as conditions are similar to those of the ordinary method: sharp local internal heating with the small wire coil, as compared with sharp local external heating with the Bunsen burner.

In the internally-heated systems of Beckmann, Richards and Matthews, and Bigelow[3] only nonelectrolytic materials can be heated. As the authors state regarding them:

The short-circuiting through the liquid causes slight decomposition, and this method is not applicable to liquids of this (the electrolytic) type.

The internal coil must be wholly immersed in the liquid, else there will be injury to the wire by overheating, with consequent decomposition of the oil, so that distillation to dryness of even low-boiling liquids is not practicable.

The internal coil partially prevents "bumping," but a fresh "boiling stone" accomplishes a like result. The boiling stone must be porous and must be fresh. If ebullition once ceases, the boiling stone seems to become less effective. Hence it is advisable, when practicable, to put a fresh unused boiling stone

[1] Beckmann, E., *Z. anorg. Chem.*, **51**, 100 (1906); *Z. physik. Chem.*, **63**, 177–215 (1908); **64**, 506 (1908).

[2] Richards, T. W., and Matthews, J. H., *Proc. Am. Acad. Arts and Sci.*, June, 1908, pp. 521–24; *Z. physik. Chem.*, **64**, 120 (1908); *J. Am. Chem. Soc.*, **30**, 1282–84 (1908); Nov., 1909, pp. 1200–2.

[3] Bigelow, S. L., *Am. Chem. J.*, **22**, 280–7 (1899)

in the cooled liquid before again heating the liquid to boiling.

The bumping is caused, the authors believe, primarily by uneven and irregular heating. Once bubbling has started, if it does not cease by reason of varying and disturbing external heat conditions, always to be considered in connection with an exposed or a gas-heated flask, or by reason of a diminution of the vacuum when one is used, the boiling will continue quietly. With the residual heavy tars and asphaltums, the internal coils are a source of annoyance in cleaning the apparatus.

When oils contain emulsified water, it is advisable during the early stages of the distillation with all forms of stills to slowly pass a dry inert gas, such as CO_2, through the still contents, by means of a capillary tube extending nearly to the bottom of the distilling flask, until the water is entirely removed. In such case it is difficult to insert the two internal conductors, a capillary tube and a thermometer through one stopper in the narrow neck of the ordinary distilling flask. To fuse the conductors through the bottom of the flask, though possible, is difficult and hardly practicable for general laboratory usage.

In short, the externally heated still described above is adapted to most, if not all, classes of laboratory work. In modified form it may be used for a great variety of heating devices. The authors recommend it to those interested.

THE CARBON DIOXIDE RECORDER AS A FACTOR IN FUEL ECONOMY.[1]

By E. A. Uehling.

Received Dec. 19, 1911.

Vast improvements have been made in power plant equipment during the past quarter century. All these improvements have been along mechanical and physical lines, consequently in the utilization of the steam, which is primarily a mechanical and physical problem, is where the great economies have been achieved.

The consumption of steam per h. p. hour has been reduced from that of 20–30 lbs. per h. p. hour less than a generation ago to 10–15 lbs. at the present time, whereas in the generation of the steam which is fundamentally a chemical problem, 30–40 per cent. of the heat contained in the fuel continues to go to waste precisely as it did 25–30 years ago. The mechanical devices, such as automatic stokers, coal elevators, ash conveyors, forced draft, etc., to be found in every large and modern boiler house, accomplish a good purpose in so far as they increase the capacity and save labor, but do not insure, or even tend to improve, combustion efficiency.

That so little has been accomplished in the reduction of waste in the process of steam generation is due to the fact that the chemist has not been called in to assist in solving the problem. It is undoubtedly stating it very conservatively if we say that not one in a hundred of the managers, superintendents and engineers of power plants know the true composition of the coal they are using. Not in one plant in a hundred are the products of combustion systematically sampled and analyzed. While it is undoubtedly true that the majority of power plant managers are aware of the fact that the boiler house is the place where very substantial economies should be realizable, they cannot get themselves to tackle the problem from the chemical side. Yet in the analyses of the flue gas lies the key to fuel economy.

Engineers as a class incline to solve their problems by mechanical means. They prefer to have something they can get at with a hammer and cold chisel and monkey wrench. Hence coal weighing machines and water meters, or water weighers, are more readily adopted than CO_2 recorders.

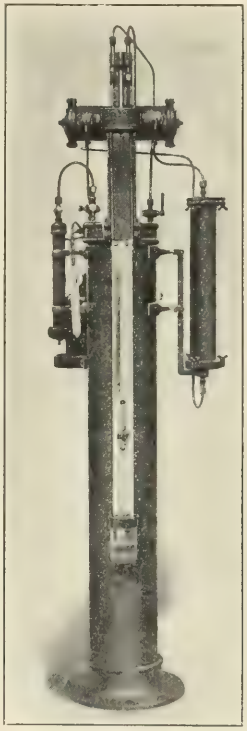


Fig. 1.

Fig. 2.

Coal and water weighing machines are a good thing to have inasmuch as they give definite information as to water evaporated per pound of coal burned. These apparatus are also useful if not absolutely necessary in testing the value of one kind of fuel against another, etc. But since you cannot solve a chemical problem by mechanical means, coal and water weighers can be of practically no assistance in attaining and maintaining boiler efficiency, which is primarily a chemical problem.

Of the heat generated from the coal burned in the average steam plant less then 70 per cent., and in

[1] Abstracted by the author from an address before the Joint Meeting of A. C. S., S. C. I. and A. E. S., New York, November 10, 1911.

many cases not even 60 per cent., is transmitted to the water in the boiler; the bulk of the balance is carried off by the products of combustion. To reduce this loss to a minimum we must know its cause, and this can be determined only by having a complete knowledge of the chemical composition as well as the physical character of the fuel used, and by keeping a continuous control over the process of combustion. I lay special stress on the continuity of control over the process of combustion, because the conditions are continually changing, not only from day to day, and from hour to hour, but from minute to minute. Changes in atmospheric condition as to pressure, temperature and humidity; changes in the physical structure of the coal as to preponderance of lumps or fines; changes in the condition of the fire, due to accumulation of ashes, formation of clinker, etc., and last, but not least, changes in the rate of combustion necessary because of variable steam consumption.

The best results are obtained in any given boiler by securing complete combustion with a minimum excess of air, and since there is a true relation between the per cent of CO_2 in the flue gas to the excess of air supplied, we have in this constituent an index to efficient firing. If, therefore, the per cent. of CO_2 be continuously revealed to the fireman it will serve as a guide and enable him to control his fire so as to obtain the most economical results.

No sane manager of a steam power plant would expect his fireman to keep up a steady pressure without the aid of the steam gauge to guide him.

Every fireman knows that his job depends on his ability to keep up the required steam pressure, and he does it. The question whether it is done wastefully or economically, although lately receiving some attention, has not been attacked by power plant managers with the vigor that its importance merits, nor from the side that promises the best results.

Fuel economy is primarily a chemical proposition and should be attacked from the chemical side. Combustion efficiency depends on so many variable conditions that a continuous control is necessary to secure the best results. Since no one would expect a fireman to maintain a steady steam pressure without a gauge to guide him, he should not be expected to maintain economical combustion without some means of knowing where he is at. The per cent. of CO_2 in the flue gas answers the requirement, and should be before the fireman as prominently and continuously as the steam pressure.

The Uehling CO_2 recorder fulfils this requirement. It consists of three principal parts: Fig. 1, the regulator or analyzer, which may be located at any convenient point within reasonable distance of the boiler, preferably in the engine room. Fig. 2, the recorder which is preferably placed adjacent to the regulator but may be put in the engineer's office if conveniently located. Fig. 3, the indicator which should be placed on or near the boiler front in plain view of the fireman. This apparatus is of very substantial construction and contains no moving parts. The gas is continuously drawn through by a steam aspirator, the CO_2 is continuously absorbed, and the volume per cent. of the gas passing through is continuously

Fig. 3.

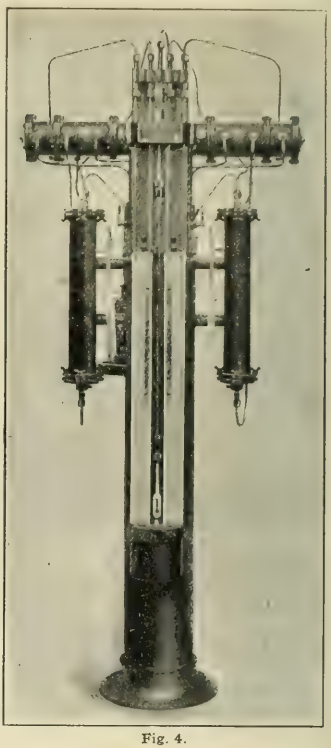


Fig. 4.

indicated and recorded. The absorbent consists of a specially prepared dry caustic soda, furnished in cartons which last about one week, and can be readily renewed in a few minutes.

These instruments are made in single, double, treble and quadruple sets either plain or in combination with pyrometers which indicate and record the stack temperature, simultaneously with the CO_2. Fig. 4 shows a double combined CO_2 and temperature recording gauge and indicator accompanying each unit.

ADDRESSES

MINERAL WASTES: THE CHEMISTS' OPPORTUNITY.

By Charles L. Parsons.

Received December 22, 1911.

No part of the world's history is more entertaining to study than the development of uses for the minerals with which we are so abundantly favored, the finding of new applications and new uses for the products prepared, and the conservation of waste material whereby the products themselves are obtained in increased quantities and at a lower cost. Such development has been a constant record of the production of new material, the applications for which have been enlarged and the demand increased by the cheapening of product through increased efficiency of method and through the utilization of other substances found in greater quantity and substituted for those which may be threatened with exhaustion.

In the earliest history of civilization only some five of our eighty or more elements were intelligently used. The number has been slowly increasing, and within the last fifty years greater progress has been made in the utilization of the mineral matter of which the earth is composed than in all previous time. The results accomplished have been the work of the chemist, the physicist, the metallurgist and the engineer, all utilizing the broad principles of chemistry to assist them in their work. Some processes have already progressed to a point where wastes are reduced to a minimum and their efficiency is great, although in no single case has perfection been reached.

The twenty-nine million metric tons of petroleum which the United States now produces is for the main part utilized. Formerly kerosene was the chief product, sought and immense quantities of the lighter and heavier fractions were allowed to waste. With the introduction of the electric light, of the automobile and of the proper understanding of lubrication, almost the total output is now worked up into gas, gasolene, naphtha, kerosene, lubricating oils, asphaltic road material and carbon for electrical purposes. Indeed, kerosene has almost become a secondary product and within the last few years the demand for gasolene has become so great that the petroleum companies are anxious to increase the output of that fraction. Indeed, the natural gas wells have introduced methods for condensing, by means of cold and pressure, the gasolene and lighter fractions carried mechanically by the gas, and during the latter part of 1910 some 13,000 gallons were so produced daily. From the gas wells from two to six gallons per thousand cubic feet of gas may be obtained and the gas itself rendered better for illuminating purposes or for gas engine combustion, but, of course, considerably decreased in volume.

Every student of chemistry knows the advances which have taken place in the iron and steel industry. Many of us can remember the old campaign arguments of how a beneficent tariff brought about the reduction in price of steel from $145 per ton to somewhere in the neighborhood of $20, but it was only in the schools that we were taught that the Bessemer process, the Open-Hearth and Basic Bessemer processes and the utilization of waste gases were the chief cause. At the present time the production of iron has reached a perfection which would have been deemed impossible a few years ago. Besides the wonderful development already mentioned the utilization of the waste gases has been carried so far that by using them directly in gas engines driving electric generators a single modern blast furnace may produce as much as 7,000 kw. of electric power besides driving the engines necessary for its own air blast.

Until recently there have also been immense losses of iron ore in the flue dust which, according to Edward M. Hager, amounted to fully three per cent. of the total ore charged. In a most interesting article on "The Utilization of the Wastes of a Blast Furnace" he points out that by collecting this dust and heating in the oxidizing atmosphere of an ordinary Portland Cement rotary kiln, this three per cent. of the ore added to the blast furnace is recovered in a nodular form carrying over sixty per cent. iron, an amount aggregating over 1,250,000, tons of iron ore per annum. Also he calls attention to the increasing utilization of slag, which formerly went to waste, for the production of a slag cement which differs but little in chemical analysis, fineness, specific gravity, color or in its operation in practical work from that made by the ordinary methods. In 1910 over seven million barrels of this kind of cement were produced in the United States, making up nearly ten per cent. of the total output of that commodity. Also hundreds of thousands of tons of scrap iron are annually collected and remelted, and improved processes for covering iron with protective coatings other than cement are making rapid progress. The wonderful effect of the growth of the Portland Cement industry on the conservation of our natural resources cannot be overestimated. In fifteen years it has developed from less than one million to over seventy-six million barrels per year for this country alone and has supplied a cheap material which not only replaces iron in much structural work but also is used as a coating to iron itself, greatly increasing its life by protecting it from rust. It is also taking the place of millions of feet of lumber, the great demand for which in recent years has been depleting our forests so rapidly. It is interesting to know that it is the thousands of small users of cement who are supplying the market for a large part of the product, and its use around the farm and the village is increasing as much as in large engineering work, such as dams, bridges and buildings. Indeed, the small cement house is becoming more and more in vogue, and with its comparatively indestructible qualities from fire or weather, together with

new methods of coloring and decorating, promises to supplant our ordinary wooden houses in future.

But the facts are seldom so favorable as those already cited. Our fertilizer industry is the largest of all our chemical industries, producing some three million tons per annum, and it is probable that one-half of this output is not intelligently utilized. We produce sulfur cheaper than any other country in in the world, sell it at the highest price and discharge into the air from a single stack of the Washoe Smelter in the form of sulfur dioxide almost as much as is utilized throughout the whole country from sulfur and domestic pyrite put together. Indeed, the total amount of sulfur dioxide discharged into the air in this country would produce probably eight million tons of sulfuric acid, the basis of all chemical industry, could it be economically recovered. That the sulfur dioxide from smelter smoke can be recovered has been proved by the zinc smelters and by the copper smelters of Tennessee, but the question is so closely connected with the question of transportation and markets that at present the idea of converting the waste sulfur dioxide into sulfuric acid seems to be almost hopeless for our western smelters, although there can be no question that in time the problem will be solved, perhaps in this way. Already rapid progress has been made and of the three million tons of sulfuric acid now manufactured in the United States, probably two hundred thousand tons are recovered as a by-product in the roasting of zinc sulfide. More than 250,000 tons are reported to have been produced in like manner from the copper smelters in Tennessee and at the same time a terrible nuisance to the surrounding farms has been largely mitigated. The fertilizer industry more than any other requires this sulfuric acid for rendering the phosphoric acid of phosphate rock available to plants, and, as immense deposits of phosphate rock exist in Wyoming and Montana, it is probable that some market for sulfuric acid will be developed in that portion of our country.

Ages ago there were stored up, chiefly through the influence of plant life, immense deposits of carbon and of nitrogen which have made modern civilization possible. Although some of this nitrogen may have been brought into combination by means of electrical discharges through the atmosphere, it is highly probable that the larger portion of it was fixed through the same form of bacterial action that is now known to take place in the tubercles growing upon the roots of the leguminosae. Certainly it appears to be true that the five hundred million tons, more or less, of sodium nitrate which is known to have been deposited in the desert of Atacama, Chili, probably is of organic origin from plants through animals whose refuse under the peculiar conditions of heat and limited water supply was oxidized and collected in this unique locality. Besides these deposits, bituminous coal contains between one and two per cent. of nitrogen, a small fraction of which can be recovered by proper methods. From these deposits, together with the comparatively small amounts which we are able to conserve by saving animal and plant refuse and returning it to the soil, we have drawn until recently our total supply of this absolutely essential element for both plant and animal food. From these supplies also we have drawn all of the nitrogen, without which we would have no explosives upon which depends our whole mineral industry. Our wastes of nitrogen, worth in combined form about fifteen cents per pound, are almost inconceivable, and no calculation can give us a real idea of what these losses mean. Their immensity has so impressed the human mind that the daily press for years has contained article after article in regard to the approaching starvation of man through the inability of the earth to supply plant life on account of the future lack of nitrogen. 2,600,000 tons of sodium nitrate are being produced each year in Chili, which means that the time of depletion of these deposits is probably less than a century ahead.

Although we produced last year over 406,000,000 tons of bituminous coal, we recovered but $3,800,000 worth of the $160,000,000 of recoverable nitrogen which it contained. Of course, it is entirely impracticable under present conditions ever to recover all of the nitrogen which might be obtained as ammonia, but it does at least seem reasonable to bemoan the fact that of 63,000,000 tons of coal converted into coke in 1910, containing $22,000,000 worth of recoverable nitrogen, only about one-seventh was even treated in ovens or retorts which could make that recovery possible. The balance went off as free nitrogen in the air. It certainly is startling to realize that if we consider the total nitrogen content of bituminous coal, last year we saved less than $4,000,000 worth of combined nitrogen from this source while more than two billion dollars worth of that stored up for us ages ago was again dissipated into the atmosphere in the uncombined condition. Of course, the recovery even of ten per cent. of this amount with our present knowledge is impossible, but it is interesting to note that the public and manufacturers themselves are being aroused to the loss, that by-product coke ovens are being employed more and more, and that the question of producing combined nitrogen from the atmosphere in which we live is making a real beginning.

As an offset to this great waste of nitrogen there are at present two essentially different commercial methods for bringing this element into combination and a third appears to be imminent. Two of these processes have already reached commercial success, but the tremendous amount of energy at present required for their prosecution raises an effective barrier against ever really offsetting the wastes which are taking place.

It is scarcely necessary before this audience to enter into detail of the processes for obtaining nitrogen in the form of cyanamide as practised at Niagara Falls and abroad or to describe again the processes of Birkeland and Eyde, of Pauling and of the Badische Company for obtaining nitric acid by means of the high temperature of the electric arc and absorbing

it in lime to be sold as calcium nitrate. It may be well to state, however, that the cyanamide is obtained by the action of nitrogen on calcium carbide heated to 1200° C., at which temperature it rapidly absorbs the gas forming cyanamide. It is necessary, however, first to produce calcium carbide and to obtain pure, dry nitrogen free from oxygen, which is done by means of liquefying air, and the cost of these operations forms the chief limitation of the process. Of the three processes for the actual burning of nitrogen and oxygen at the elevated temperature of the electric arc the Birkeland and Eyde process at Notodden, Norway, has been so far the most successful, perhaps because it was the first in the field and has cheap electric power. This last year they utilized some 50,000 kw. of electricity throughout the year which is to be increased to 100,000 kw. Their output approximates 70 grams of HNO_3 per kw. hour and their furnace has the great advantage of being capable of use in large units, some of which are of 4,000 horse power. They report net earnings for this last year of some $350,000 and produce nitric acid as calcium nitrate, which commands a ready market. The Pauling process is being used near Briancon, France, and also appears to be in successful operation. The Badische process is to be installed in new works in Norway together with the Birkeland and Eyde process and it is estimated that the two processes will shortly be using 250,000 horse power in that country.

Even this tremendous expenditure of energy can, however, supply but a fraction of the world's requirements for combined nitrogen, as it requires one kw. year to produce one ton of 13 per cent. calcium nitrate. The success of these processes at the present time is dependent almost solely on the question of cheap energy. The principle of all is the same; namely, the utilization of the intense heat of the electric arc to bring about a reaction between nitrogen and oxygen and the quick cooling of the gases in order that the reaction may not reverse itself. In the Birkeland and Eyde process the electric arc is branched out by means of an electric field; in the Badische process a similar active surface is obtained by producing long arcs even up to twenty-two feet in length in tubes, and in the Pauling process the arc is enlarged by means of a blast of hot air under pressure. Patents recently issued to the Badische Company indicate that an entirely new method may soon be used, depending upon the reaction between nitrogen and hydrogen under pressure with the reaction hastened by uranium or some catalytic agent, the ammonia being absorbed as fast as produced. It will certainly be of inestimable advantage to procure some method by which nitrogen can be fixed without the tremendous loss of energy required when it is heated to the 3500° required in the electric processes. It would certainly seem that if bacteria can bring about the fixation of nitrogen in the small laboratory they utilize on the roots of the legumes, man must sooner or later also succeed in bringing about this reaction at moderately low temperatures, and I confidently believe that we may in some measure hope in time to imitate this process through the use of catalytic agents.

The waste of our fuel supplies is almost inconceivable. In the mining of coal in this country it is probable that scarcely 50 per cent. of the coal in the ground is taken out and brought into a form where it can be economically utilized. That portion which is left behind is undoubtedly lost forever, for the mines are allowed to cave in and probably can never be opened again. Of the energy in the coal mined probably not over 11 per cent. is effectively utilized. The remainder of the energy is lost through the inefficiency of the steam boiler, the steam engine and the electric dynamo. It is estimated that the boiler scale alone on the locomotives of the country means a loss of over fifteen million tons of coal. It has been shown that $^1/_{16}$ of an inch of boiler scale means a loss of 13 per cent. of efficiency and that $^1/_8$ inch, which occurs in many boilers, means a loss of 25 per cent. Not only does this boiler scale mean a loss of energy, but its removal means much longer life for the boilers themselves.

The whole question of the conservation of these losses of energy is becoming almost as much the province of the chemist as of the engineer. In spite of present conditions, great advancement has been made and greater advances are yet to come, although the time when we shall be able to directly utilize the full energy of carbon through some direct chemical process may not be reached before the millenium is here.

Our supplies of coal are being more and more conserved directly through the utilization of water power, of which, according to M. T. Bogert, there are 150,000,000 horse power possible of economical development in this country, of which 37,000,000 horse power, equivalent to 800,000,000 tons of coal, are readily available and of which 5,500,000 horse power are now actually used. Also the development of the gas engine, by means of which power can be obtained without the intermediary loss through steam, is rapid and has the distinct advantage that much coal, too poor in carbon content to be economically transported, can be readily used in gas producers and its energy utilized and transmitted to a distance through the gas engine and dynamo. The covering of pipes with asbestos and magnesia coatings and the scientific control of the combustion of coal under boilers is adding greatly to the amount of energy actually utilized. Also, as already stated, the recovery of waste products through by-products coke ovens is not limited to the nitrogen alone. Mr. E. L. Parker, of the United States Geological Survey, states that the value of the recoverable contents of the coal made into coke in beehive ovens which went to waste in 1910 would have been worth between $35,000,000 and $40,000,000. If all the coke made in the United States was produced in retort ovens, these would yield (from the carbon now wastefully consumed) without reference to the other by-products obtained approximately 1,000,000 horse power for every day in the year.

Without entering at all into the detail of the wonderful coal tar industry, which has not as yet been developed in this country, but is probably the greatest example of chemical industrial progress, it is interesting to note the indirect bearing upon our conservation which this coal tar develops when we think of the alizarin, indigo and other colors which were formerly produced on land now devoted to other purposes. It has been stated that the synthetic indigo now prepared from coal tar is equivalent to over 300,000 acres of indigo plants. Development of one industry like this always has a striking influence upon another. When the cyanide process for the extraction of gold was first proposed potassium cyanide cost over one dollar per pound. By the utilization of waste products and the perfection of methods the price of cyanide, now chiefly used in the form of sodium cyanide, has been reduced in the chief producing countries to something like fifteen cents per pound and since a difference of one cent per pound of cyanide means a saving of something like $150,000 a year to the gold industry, the cheapening of this product alone means a saving of some $12,000,000 a year.

In spite of the losses through waste already mentioned and many others that might be cited, there is really a silver lining to the cloud. When we look at the question from the standpoint of the progress that we have made and the problems which may perhaps be easily solved, we feel proud of the work which the chemist has accomplished and glad that we belong to a profession which offers so much in the way of accomplishment. The president of our largest chemical corporation recently stated that progress in chemical industry is taking place so rapidly through new processes, new machinery and new methods that his company has very little in the way of plant to-day which was in existence ten years ago. Only three years ago one of our leading scientists stated: "The crest of our known resources of high-grade copper ores is clearly past and we are using lower and lower grades with increased cost of production. The inadequacy of our copper supply is a matter of deep concern." This, of course, is largely true, but the situation has developed in a different way from that indicated by the quotation given. The fact is that the low-grade ores are proving the more profitable to work and have not brought an increased cost as might have been anticipated. Indeed, although our production of copper has increased about one thousand per cent. in the last twenty-five years, the annual output as well as consumption is still increasing and prices are lower than they were three years ago, owing to the greater efficiency of method and the utilization of deposits formerly supposed to be worthless. Immense mountains of ore yielding less than 2 per cent. of metal are worked with steam shovels, concentrated in mills capable of handling some 30,000 tons per day, with a recovery three years ago deemed impossible, smelted by methods far more efficient than those then in use, and bessemerized in basic-lined converters capable of handling three times the charge of the old acid form, using some ore direct for its fluxing constituents and having a life many hundred per cent. greater than their forerunners. These low-grade deposits, instead of causing an increase in the price of copper, are really forcing some of the high-grade mines to struggle for a continued existence. In spite of all this, it is doubtful if there is any branch of our metallurgy that would respond more quickly to scientific research by well trained men, who were not forced always to keep the immediate output in mind, than the metallurgy of copper.

But our industrial chemical problems are not all connected with the larger industries of which I have so far spoken. Many new elements, many new minerals and mineral products, are coming into daily use and have also their minor problems in the question of the utilization of waste. In the manufacture of thorium for the Welsbach mantle the larger part of the raw material present in the original monazite now goes to waste. About 50 per cent. of this is cerium and the balance lanthanum, neodymium, praseodymium and other rarer elements of the rare earths. There is every prospect that the cerium will soon be utilized and bring a fair price. Its separation from the other earths is no longer difficult and once in solution can be brought about in a single operation. Its properties in alloys, some of which have most remarkable pyrophoric properties, are now well known and the metal can be readily reduced by the electric current. The oxide of cerium as well as the oxides of the other elements that occur with it are highly refractory and may find special uses where this property comes into play.

In the production of gold telluride ores and in the refining of copper, large amounts of tellurium are annually going to waste and offer a splendid opportunity for research. No promising application is yet in view.

Our output of bromine might also be greatly increased could uses be found. The application to the formation of bromides is apparently not increasing, but there seems to be a real opportunity for its use in the form of bromates and it would appear that potassium bromate, the wonderful oxidizing properties of which are not yet appreciated, may have a real use in metallurgy and possibly in other industries when it is more clearly understood that if a real demand arises the material can be furnished at a surprisingly low cost. Indeed, many of our rarer elements are being passed by in the industries chiefly because the cost of production on a small scale is much greater than would be the case if an extensive contract could be entered into. Also manufacturers themselves frequently prefer to let large quantities actually go to waste rather than reduce their prices in order that the wastes may be utilized.

Chlorine, like bromine, is produced in the electrolytic manufacture of caustic soda and potash in amounts which make its utilization a problem. It is being worked up more and more into the form of by-products such as carbon tetrachloride, sulphur

chloride and acetylene chloride, is being liquefied and transported in liquid form for the direct production of sodium hypochlorite for use in laundries, and is utilized in recovering the tin from tin scrap in the form of tin tetrachloride used chiefly for weighting silk. It can now be obtained in cylinders which are so cheaply made that their return is not necessary, or it can even be procured, if desired, in tank cars.

Bleaching-powder also, by being mixed with a little copper sulphate and cobalt oxide to act as a catalytic agent, is now on the market as a cheap source of oxygen under the name of Lavoirsite.

Calcium also can be readily obtained cheaply and in quantity as soon as a use therefore is found.

Silicon, which has some wonderful properties of resistance to chemical agents, is now easily made and except for its brittleness would probably find extensive use. Even as it is, uses are gradually developing, one of the most interesting of which is for the shoes of the plows used in certain acid or pyrite furnaces where iron rapidly goes to pieces. Many tons of this element are used in alloy with iron, especially in electrical transformers. It reduces hysteresis losses and increases resistance.

Among the comparatively rare elements and minerals which are becoming more and more prominent in industry may be mentioned tungsten, the ores of which to the extent of some 6,000 tons per annum are now worked up, to be used chiefly in the production of tungsten steel but also in the filaments of electric lamps; vanadium, for the preparation of vanadium steel; titanium, for the preparation of ferro-titanium, with which more than half of the Bessemer steel now produced is treated in order to deoxidize and denitrogenize the product; and selenium, obtained as a by-product in copper refining, which has the unique property of changing its conductivity under the influence of light and which is now used to the extent of some twenty tons per annum to color glass or enamel a beautiful ruby-red, and also by use in small amounts to decolorize glass or enamel by neutralizing the greenish tint from ferrous iron.

Bismuth, so valuable in medicine and alloys, is now obtained as a by-product in the electrolytic refining of lead in this country alone to the extent of some 90,000 pounds per year. Palladium even is finding new uses, so that the accumulated supplies of many years appear to have been exhausted and it is being recovered to the extent of 2500 oz. per year from copper anode slimes. Zirconium oxide is being eagerly sought for and new patents issued almost daily for its use and production, chiefly on account of its refractory properties and its power to replace tin oxide as an opacifier in enamels. Magnesium even appears to have a future in certain very light alloys of high tensile strength for use in the constructions of aeroplanes. It is stated that the alloy with 4 per cent. of zinc is extremely light and extremely strong. Also magnesite is greatly in demand for the preparation of refractory brick, but unfortunately no deposits are known in this country east of California. On our Atlantic coast at least, most of it must be imported, although immense quantities exist, together with calcium carbonate, in dolomite.

Barium in the form of barite, with the products therefrom, is finding an increased use in paints and in the production of barium sulfide for the manufacture of lithopone. Barium dioxide is imported for use in the manufacture of hydrogen peroxide, since America has no deposits of witherite.

Lithium carbonate is also now a comparatively cheap substance that could be produced in much greater quantities if more extended uses could be found.

Asbestos is eagerly sought and its technology has become so extensive and its uses so diversified that an article could be written on this subject alone. The application to fire-proof asbestos lumber, which can be sawed and milled, and to asbestos slate, which is replacing shingles, is having the advantage of utilizing the cheaper grades which were formerly largely a waste product. The same may be said of mica, and the old mica scrap heaps at the exits of old mines have been all carefully reworked on account of the excellent insulating material they contain as well as for the production of other products in which scrap mica has been utilized. New methods are also rendering available much material that formerly went to waste and are also cheapening and thereby increasing the application of much other material long used.

Immense deposits of graphite have not been available on account of the impossibility of separating them from the gangue that they contained, but it has been found that in many cases simple pulverizing and sifting through sieves will separate the fine granular gangue from the more flaky graphite.

Immense deposits of molybdenum occur in Maine and in the West which have been useless for the same reason. They could not be worked unless they could be separated from the gangue and no good method of separation was known. Molybdenum has not been used extensively in steel chiefly for the reason that tungsten, which served the same purpose, was cheaper, and also molybdenum has the disadvantage of volatilizing out of the steel quite easily. On the other hand, a much smaller amount will bring about much the same result that tungsten produces. Manufacturers have been willing to pay as high as $600 per ton for limited amounts of good molybdenite, practically all of which had to be imported. By a new flotation method it now seems possible to separate molybdenum as well as other sulfide ores from the inert material with which they occur, and it is hoped that our American resources of this mineral may now be utilized.

Considerable deposits of carnotite and some uraninite are found in Colorado, and the material is now being exploited for the extraction of radium abroad. In view of the immense value of radium for scientific and medical purposes, it would certainly seem that this wonderful substance should be produced in our own country, and it would at least seem pos-

sible that some more rapid method for its separation might perhaps be found. The production in France for 1910 was something less than two grams, which sold for $150,000, and the material is so rare that in Paris one hundred milligrams is rented out at the rate of one hundred to two hundred dollars per day for scientific or medical use.

The new method of following the wastes of zinc concentration in New Jersey by means of ultra-violet light is also of extreme interest, and it is stated that the wastes, which formerly amounted to some 5 per cent., have been reduced to less than 2 per cent. with the assistance of this method.

Much might be added on the question of alloys, artificial stone, refractories, nickel and cobalt, arsenic, antimony, tantalum, boron and beryllium, but I do not wish to try your patience too far.

In order properly to cultivate our natural resources, experience has taught our progressive manufacturers that two kinds of trained chemists are essential if they expect to keep ahead or even abreast of the world's progress. They must have the works laboratory where careful control is kept of the actual carrying out of the process in hand, and they must have a research laboratory where new processes, applications and ideas are developed and the efficiency of old methods studied with a view to greater economy of production and value of output. The importance of the works chemist has long been realized, and his usefulness is continually augmented by the fact that customers are becoming more and more exacting in their requirements for purity of product and more and more insistent that standard specifications be accepted and fulfilled. The research chemist has until recently been appreciated only in Germany, but America is fast awakening to the real basis of Germany's industrial progress and research laboratories are now installed by large numbers of our most progressive producers.

It is probable that the first American commercial laboratory where the real spirit of research was fostered by the company itself was established less than ten years ago. To-day there are over fifty in active operation with a steadily increasing corps of investigators, and one at least has passed the hundred mark for the number of chemists employed. These laboratories have justified their existence and in every instance where properly trained men have been secured have returned the investment many fold. Better still, they have kept their respective firms far ahead of their competitors. Other corporations, less wise in their understanding of the requirements of the situation, have thought they were establishing laboratories when they employed some recent graduate at one-tenth the salary they would pay their engineer and one-fiftieth of that they would allow their lawyer and have expected him to revolutionize the business within a twelvemonth and act as foreman and analyst meanwhile. Sometimes even then *they* have drawn a prize. Research laboratories are also being fostered by the government and by educational institutions. Even a few of our more progressive consulting laboratories are supporting research departments. This can have but one result, which is that American industry is not to depend alone upon unlimited natural resources, but also upon new and increasingly efficient methods for their development. Indeed, specific instances of wonderful accomplishment are not rare, although secrecy as to results is too often insisted upon and maintained.

A few instances may prove of interest. A chemist of my acquaintance had been employed for years by a large textile company that saw no need for chemical research and kept him confined almost wholly to passing upon the quality of the supplies they bought. It happened that this company's engineers installed an open pipe line through which raw cotton was blown from mill to mill and which proved a great saving over the previously used mode of transportation. Their plan worked beautifully until the cold days of the late fall arrived, when moisture on the cotton from the warm mills condensed and freezing to the large galvanized pipes soon caused a stoppage. This was removed, to be immediately repeated, and it was evident that something must be done or the plan abandoned for at least five months of the year. By chance, this chemist was standing by when advice was given by the local engineers to box in the pipes and heat with other pipes carrying steam. Knowing some of the principles of elementary physics, he modestly suggested that instead they open the window that happened to be near and blow with cold air inside as well as outside the pipes. Of course, there was then no condensation of moisture, the pipes worked equally well the year round and some $14,000 of construction was rendered unnecessary. A little later a specially fine grade of cloth appeared to demand a treatment which the foreman stated could be done only by hand, and plans were drawn for a new building to accommodate seventy additional laborers for the purpose. Profiting by experience, the general manager, for perhaps the first time, called his chemist into conference, with the result that the plans were temporarily held up and after a few weeks finally abandoned, for a chemical treatment was accomplishing easily, cheaply and rapidly the work of seventy men. It is useless to follow the case further except to say that in at least one other instance since he has to my knowledge saved in a single year's operation of a new process more than the company will pay him in his lifetime. He is now appreciated by his employers and recompensed in some measure of his value to them, and his work is now of a research character with helpers for the routine.

In another instance the vice-president of one of our large corporations told me that in the first year their research laboratory was established one thing accomplished alone netted the company $80,000. Furthermore, he added that this was only one of a dozen improvements, each one of which more than paid for the total running expenses of their research work.

In another case of which I know, a young and well trained chemist was sent by his company to Amsterdam to make a special study of the phase rule under Roozeboom. They were manufacturers of soap, and a special brand they made was subject to great fluctuation in cost through the varying price of one of its constituents. On his return to the laboratory he was able to apply the new knowledge he had gained in such a manner that he shortly drew a chart, intelligible even to the foreman, by which certain substitutions were made as the market varied without altering, in any way, the physical character of the product, a result which had before been impossible. In the first year something over $90,000 was saved thereby.

While these are only a few of the cases of which I have personal knowledge, one has only to read the exceedingly interesting address of Dr. W. R. Whitney on "Research as a Financial Asset" to be immediately convinced that no other asset is more promising for investment. He casually mentions the fact that although the expense of the research laboratory of the General Electric Company is now considerably in excess of $100,000 a year, it has been a good expenditure of money. As the result of the work on improvement in incandescent lamps alone, very largely brought about in his laboratory, some $240,000,000 a year are saved to the consumers of electricity by the greater efficiency of operation. He mentions also another case where a corporation had saved by the results of its research men over $800,000 a year and cites many other instances minor only by comparison.

In closing, I want again to call attention to history and sound a warning to all young chemists here to-night. It has often been said that the reason that Germany has forged so far ahead of England in her industrial development is that German manufacturers have always appreciated brains and that pure scientific research has been encouraged to go hand in hand with the industry. England, on the other hand, has believed in the "practical man" and their manufacturers have had little sympathy with the theoretically inclined. In America we have both kinds, not only among our manufacturers but among the chemists they employ. Many are coming nearer to the German idea and they are the ones that are succeeding.

As Secretary of the American Chemical Society, I have many queer experiences, but none have proved more enlightening than letters received and conversations held with certain industrial chemists on the one hand who laugh at the phase rule, the mass law and the general application of advanced theory and who openly state that they believe the *Journal of the American Chemical Society* is a waste of good paper, while on the other hand certain so-called pure scientists, too often speaking from a pedestal raised by themselves and their admirers, sneer at the application of their own science and consider them and the journal in which they find place quite unworthy of their time and notice. Fortunately the number of each is small and is decreasing. I am sure there are none such in this audience, but I am sure that in so far as your knowledge of the theory of our science is complete and your ability to apply your knowledge develops, just so far will you measure up as a successful man.

Our science has progressed so far that each one of us must specialize to cover, even passably, our particular field, but this can never excuse us for a lack of sympathy with our honest co-workers. It is only arrogance and ignorance that assume omniscience.

PERKIN MEDAL AWARD.

The Perkin Medal was conferred, December 19th, in Rumford Hall, Chemists' Club, New York, on Mr. Herman Frasch for distinguished services in the fields of Applied Chemistry.

Mr. Frasch's inventions in connection with the purification of sulphur oils of Canada and the Ohio field, and also his invention of a method and the development of the mining operations in the sulphur fields of Louisiana, are fully discussed in the Presentation Address by Professor Chandler, and the acknowledgment by Mr. Frasch. An additional feature of the program was an address on the "Geology of the Sulphur and Sulphur Oil Deposits of the Coastal Plain," by Captain A. F. Lucas, and an address by Mr. F. H. Pough, of the Union Sulphur Company, on the operations of their mines in Louisiana. Mr. Pough's address was illustrated by lantern slides and moving pictures taken at the sulphur mines as late as Saturday, January 13th.—[EDITOR.]

INTRODUCTION.

By M. C. WHITAKER, Chairman.

The Perkin Medal, established to perpetuate the memory of the founder of a great chemical industry, is again to be awarded for distinguished service in the field of applied chemistry. Sir William Perkin expressed deep appreciation to his fellow workers in America for the honor paid him on the occasion of its establishment. The full wisdom of the plan is slowly unfolding to us as we see, year after year, our chemists gather in these halls to single out and honor a distinguished member of our profession.

A committee representing the chemical organizations of America, a body of men selected for their wide knowledge and experience in chemical and industrial development, deliberate and select. Merit and achievement alone determine their choice.

Dr. Chandler, we present to you, as the Past President of the Society of Chemical Industry, and as the officer wisely designated in the rules of the Society to make the presentation address, the unanimous choice of the committee. You, better than any other member of our profession, can speak with knowledge and with admiration of the scientific achievements of our distinguished guest of this occasion, Mr. Herman Frasch.

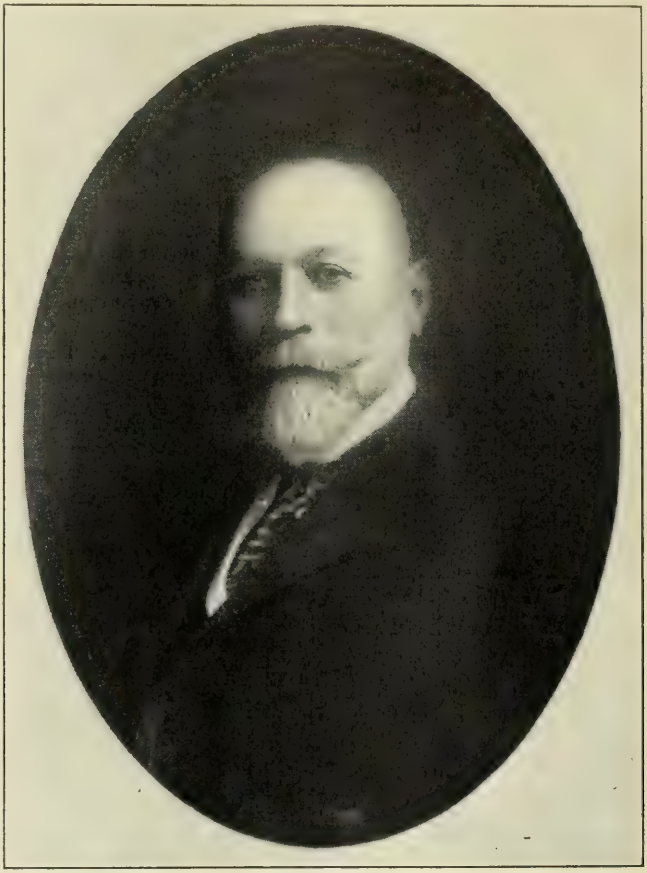
PRESENTATION ADDRESS.

By C. F. Chandler

Mr. Chairman, Brother Chemists, and Mr. Frasch:

It is my very pleasant privilege as the senior Past President of the Society of Chemical Industry, residing in this country, to present to Mr. Herman Frasch, on behalf of the Perkin Medal Committee of the Associated Chemical and Electro-Chemical Societies of America, the sixth impression of the Perkin Gold Medal, in recognition of his most valuable work in Applied Chemistry.

Herman Frasch was born in Gaildorf, in Wuertemberg, in 1852. In 1868 he took up the practice of Pharmacy, came to America, and was placed in charge of the laboratory of Professor Maisch at the Philadelphia College of Pharmacy. He found, however, that Industrial Chemistry interested him much more than Pharmaceutical Chemistry, and in 1874 he established a laboratory of his own. Here began the studies and investigations which resulted in some of the most important achievements ever accomplished in industrial chemistry.



HERMAN FRASCH,
PERKIN MEDAL 1912.

In 1876, at the age of twenty-four, he evolved a process for refining paraffin wax which was purchased by a Cleveland Petroleum Company, affiliated with the Standard Oil Company. These companies were so well pleased with his first invention that they induced him to give up his work in Philadelphia, move to Cleveland, and make the petroleum industry his specialty. He devoted himself assiduously to the refining of petroleum, and made many improvements in the processes in use, for some of which he sought and obtained patents. The first was applied for December 15, 1876, when he was but twenty-four years of age. It was for an improvement in apparatus and processes for the separation and treatment of oils, by more completely separating the more volatile constituents from the less volatile, in order to increase the density, improve the fire test, sweeten the odor, and otherwise improve the quality. This was followed by further applications for additional improvements for the same purpose. Five such patents were applied for between 1876 and 1885, all of which were granted.

He also obtained a patent in 1884 for the manufacture of waxed paper, a material saturated with paraffin which has found a great variety of applications. In 1885, Mr Frasch invented an improved petroleum oil lamp.

Our great inventor's attention was not, however, confined to petroleum. In 1882 he invented a process for manufacturing white lead directly from the Galena ore. In the same year he devoted considerable attention to improving the processes and apparatus for manufacturing salt, a subject which continued to occupy his attention for several years. Five patents for his improvements in this industry were applied for in the years 1882 to 1899, and subsequently granted.

He also studied the ammonia process for making carbonate of soda from salt, and between 1882 and 1886 applied for four patents for improvements, all of which were granted.

In 1883 Mr. Frasch devised a very ingenious invention of a process of making elements for thermal electric generators, which was granted the same year. In the same year he obtained two patents for the manufacture of a superior carbon for electric light carbons, and carbons for other purposes, from "wax tailings" or "still wax" by treating the same with nitric or sulphuric acid in a specially designed furnace.

Mr. Frasch's contracts with the various oil companies expired in 1885, and he then moved to London, Ontario, where he went into business for himself, forming the Empire Oil Co. It was here that he

solved the Canadian oil problem, by devising a simple process by which the offensive oils of Canada and Ohio could be made so pure that they became as valuable as the Pennsylvania oil. There had never been any difficulty in treating Pennsylvania oil so as to obtain perfectly sweet gasolene, benzine, naphtha, burning oil, lubricating oil, and paraffin, for the simple reason that these oils were practically free from sulphur. But the Canadian and Ohio oils contained about one per cent. of sulphur, in such offensive combinations that it was impossible to obtain from them, by the customary processes of treatment, products that could be marketed, so they were only available for fuel purposes. Many chemists attacked the problem of deodorizing those oils by decomposing the sulphur compounds; many processes were devised and patented, but not one of them was satisfactory until Mr. Frasch began to study the subject. On February 1, 1887, he applied for his first patent for "Refining Canadian and similar Petroleum Oils," and by December 31, 1894, had applied for twenty patents for his inventions in connection with this subject, all of which were granted. The essence of his invention consisted in distilling the different products of the fractional distillation of the crude oil, with metallic oxides, especially oxide of copper, by which the sulphur was completely removed, by entering into combination with the copper, while the oils distilled over as odorless and sweet as those from the best Pennsylvania oil. The process was comparatively inexpensive, as Frasch devised simple processes for separating the sulphide of copper from the residuum, and restoring it by roasting to its original condition, making it possible to use it over and over again on fresh lots of oil.

It was in the works of the Empire Oil Co. that Mr. Frasch solved the problem of raising the terribly offensive sulphur-containing oils of Canada and Ohio from the low grade of fuel oils, to the highest grade of purest oil. He had the process in operation on a large scale, when in May, 1888, the Standard Oil Co. purchased his patents after they had been thoroughly investigated and tested by their experts. The Company bought the works of the Empire Oil Co. at London, Ontario, and proceeded at once to construct large works for carrying out Frasch's inventions at Lima, Cleveland, Whiting, Olean, Philadelphia and Bayonne. Mr. Frasch received in payment, stock of the Standard Oil Co. selling at that time for 168 and paying 7 per cent. After his process had been thoroughly established, he sold half his stock at 820, and the Company had been paying for some time 40 per cent. instead of 7 per cent.

When one considers that the capital of the Standard Oil Co. was one hundred million dollars, the pecuniary return from the Frasch process in the increased value of the stock, and the greatly increased dividends, assumes gigantic proportions.

In addition to the advantages to the owners of the stock of the Standard Oil Co., there were a host of others who profited to an enormous extent. Frasch's process sent up the price of crude Ohio oil from 14 cents a barrel to $1.00 and above, thus benefitting the farmers and oil producers of Ohio, Indiana and Illinois; and also by greatly increasing the demand for this kind of oil, until the production of this field went up to 90,000 barrels per day, giving an increase in return to the land- and well-owners of untold millions of dollars.

Other inventions of Mr. Frasch in connection with petroleum refining are:

1890.—A process for removing from the heavier burning fraction of the oil, the sulphuric acid taken up during the acid treatment by the cracked products. This he accomplished by distillation with lime.

1895.—Processes for increasing the flow of oil wells. The Pennsylvania oil wells occur in the Devonian sandstone, and in order to rejuvenate an exhausted well, it had long been customary to shatter and crack the surrounding rock by exploding one or several hundred quarts of nitroglycerine at the bottom.

In Ohio, Indiana and Illinois, the wells occur at a much deeper geological horizon, in the Silurian limestones. Frasch substituted sulphuric or hydrochloric acid in place of nitroglycerine for the purpose of rejuvenating the exhausted wells, one proving best in some localities, the other in other localities, as one yields insoluble calcium sulphate, and the other soluble calcium chloride.

By plugging the wells after the acid has been poured down, the pressure of the carbonic acid gas forces the acid through the most minute cracks, which were thus widened so as to open communication with new cavities of supply.

1900.—The application of live steam to remove completely the gasoline, naphtha and benzine from the burning oil in the process of distillation, in order to raise the fire tests.

1902.—A process for treating the peculiar crude oil of Fresno Co., California, so as to remove the valuable aromatic hydrocarbons which it contains: Benzol, toluol, xylol, mesitylene and naphthalene.

1902.—A process by which it is made possible to secure a satisfactory burning oil, from the peculiar crude oil of Beaumont, Jefferson Co., Texas, which consists on washing out of the burning oil fraction, its peculiar smoke producing hydrocarbons, by means of wood alcohol.

1899.—Improved processes to bring to the surface by solution, the rock salt reached by boring.

1894.—Process for purifying solvent extracted oils, having special reference to linseed oil, consisting in removing the solvent naphtha from the oil by low tension steam in a partial vacuum.

1895.—Improvements in mining gold or like metal, which consist in saturating strata containing the diffused metal with an aqueous solution of a suitable solvent, the final solution being subsequently drawn from wells or borings through the strata.

On the 23rd of October, 1890, Mr. Frasch applied for a patent for an epoch-marking improvement in the sulphur industry. It had long been known that there was a large deposit of native sulphur in Cal-

caster Parish, Louisiana, at a depth of one thousand feet below the surface. But all attempts to get at the deposit and bring the sulphur to the surface had failed completely, on account of the layers of quick sand above the deposit. Mr. Frasch evolved the idea of melting the sulphur in place, by means of superheated water forced down a boring, and forcing the melted sulphur to the surface, through an inner tube. During the period beginning October 23, 1890, to February 6, 1905, Frasch has applied for ten patents for his inventions of apparatus and processes for accomplishing this result.

His efforts have been entirely successful. The Union Sulphur Co. was organized, he secured control of the sulphur deposit, set up the batteries of boilers, bored the wells, built the railroad to carry the sulphur to the seaboard, and the docks at Sabine Pass, for the ships which deliver the sulphur to the seaboard.

There are seven batteries of boilers, each of which runs a well. A single well delivers about four hundred and fifty tons of sulphur per day. In a two-months test, six wells delivered one hundred and twenty-two thousand tons of sulphur, proving the capacity of the mines to exceed the entire consumption of the world.

The sulphur is pumped into bins about fifty feet high constructed of planks, where it congeals and forms a block of from seventy-five thousand to one hundred and fifty thousand tons, over ninety-nine per cent. pure sulphur. The planks are subsequently removed, the huge block is broken up by blasting, and the sulphur is loaded directly into the cars by a scooping derrick which picks up two tons at a time.

The effect of this work on the imports of sulphur into the United States is very far-reaching, as will be seen in the following figures, showing imports and exports of sulphur into and from the United States.

	Imports. Tons.	Exports. Tons.
1903.....	188,888	none
1907.....	20,399	35,000

At present the Louisiana Deposit supplies this country with sulphur, and might supply large quantities to European countries. Fortunately the Company is owned by a few broad-minded and large-hearted men, who could not be induced to bring starvation and ruin upon the two hundred and fifty thousand people dependent upon the mining of sulphur in Sicily.

Ninety per cent. of the stock of the Union Sulphur Co. is owned by Herman Frasch, the estates of H. McK. Twombly, Abram H. Hewitt and Edward Cooper and Mr. L. H. Severance.

I have presented to you very briefly the great achievements of Mr. Frasch in the field of Applied Chemistry, but quite fully enough to satisfy you that your Committee is fully justified in placing Mr. Frasch by the side of Sir William Perkin, as one of our greatest Industrial Chemists and Chemical Engineers.

To Mr. Frasch:

It gives me great pleasure, as the representative of the Society of Chemical Industry, and the affiliated Chemical and Electro-Chemical Societies, to place in your hands this beautiful token of the appreciation and affection of your Fellow Chemists.

ADDRESS OF ACCEPTANCE.

By Herman Frasch.

Mr. Chairman, Ladies and Gentlemen:

When I received the notification that I had been awarded the Perkin medal, I was most happily surprised. I recognize and appreciate fully the honor and distinction which the medal conveys, and I wish to express my sincere thanks and appreciation to the members of the Awarding Committee and to the Societies which they represent.

OIL.

Very little is known of the impurities contained in petroleum. They influence the price, however, to a remarkable degree. The best illustration of this is the case of Ohio oil. This contains about 0.75 per cent. of sulphur, and before my desulphurizing process was known sold at 14 cents per barrel, while Pennsylvania oil, with a sulphur content of only 0.03 per cent., sold at $2.25 at the same time. Sulphur affects the value of petroleum in a greater degree than phosphorus does that of iron ore.

One of the oils which contains an objectionable amount of sulphur is that found near Pretolia, Ontario. It is the only crude that has been found in the Dominion of Canada. When this oil was first discovered in 1868, it was refined in the usual way—treated with sulphuric acid and soda, and then put on the market. The result was disastrous. The odor emanating from the oil was very offensive and penetrating, so much so that the cargoes of ships carrying flour and bacon, anchored near a vessel loaded with Canadian oil, were spoiled, as the flour and bacon absorbed this odor. Law-suits based upon these facts were decided against the shippers of Canadian oil, and all export ceased. In order to protect the home industry, the Canadian Government imposed a duty of 9 cents per gallon on Pennsylvania oil, but in spite of this almost prohibitive duty, half the oil consumed in Canada was imported from Pennsylvania.

The offensive odor of this oil, moreover, was not its only objection. It had also the property of depositing soot upon the lamp chimney, so that a large percentage of the light emitted by the flame was lost.

The Canadian Government, as well as the Canadian producers and refiners, made every effort to discover a method by which the objectionable properties of this crude oil could be eliminated, but practically nothing has been accomplished in twenty years, except perhaps in the matter of covering up the odor, when in 1885 I bought a refinery in Canada and made a thorough investigation of the character of this crude and decided to discover a remedy, if possible.

This dreadful odor, which the Canadians called "skunk," arose from a peculiar hydrocarbon-sulphur compound, and the clouding of the lamp chimney was due to its sulphur content. The sulphur in the oil burned into sulphuric acid, which condensed against the lamp chimney, and any unconsumed carbon of organic particles in the air would adhere thereto and form this objectionable soot. To remove the sulphur from the oil completely meant the elimination of the smoke as well as odor, and when this was effected the oil furnished an illuminant equal in quality to the best Pennsylvania.

To free petroleum of elementary sulphur or hydrogen sulphide presents comparatively little difficulty, but the sulphur compound which is the cause of this offensive odor is very stable and cannot be broken up into hydrogen sulphide or any other sulphur compound which can be eliminated. It was because of the presence of this peculiar compound that Canadian oil for so many years resisted all the efforts made to refine it.

This sulphur compound has the peculiarity of dissolving a number of metallic oxides. When the oil is saturated with all the oxide it can carry in solution, the disagreeable odor disappears. It reappears, however, if an attempt is made to free the solution of its metal. I found that this solution of metal in petroleum has an intense affinity for sulphur, and also that when a portion of the sulphur has been precipitated with the metal as a sulphide, additional quantities of metal oxide can go into solution. If more oxide than that necessary to precipitate all the sulphur is added to the petroleum while it is being distilled, a complete desulphurization of the petroleum is effected.

When this petroleum solution is made with water-white petroleum distillate, which has been freed of elementary sulphur and hydrogen sulphide, the solutions assume colors characteristic of each metal. The lead solution is a canary-yellow; mercury, orange; copper, blood-red; silver, brown.

I selected copper as the metal most suitable—first because it dissolves in the petroleum, and in the second place because of the readiness with which the sulphide of copper can be reconverted into oxide.

When the laboratory work had been completed, I applied for letters patent and erected a 1,200 barrel still, carrying on the process on a large scale. The shell of the still was 22 feet in diameter and 16 feet high, and was supplied with a stirring device which kept the copper in suspension while distillation was carried on. After 80 per cent. of the contents of the apparatus was distilled, the remainder, when cool, was pumped through a filter press. The solid portion was ignited and roasted, while the liquid residuum was mixed with a new charge of revivified oxide of copper to be used for the desulphurizing of a further quantity of sulphur-containing distillate. I used a shelf furnace, operated by hand, to roast the resulting sulphide of copper. In this manner I produced a burning oil containing 0.02 per cent. sulphur, which is the percentage contained in Pennsylvania oil of similar specific gravity, while Canadian oil, refined by the ordinary method, has a sulphur content of 0.6 per cent.

It was about this time that oil almost identical with the Canadian was discovered in Ohio, and while the question of refining Canadian oil was interesting, the problem became intensely important when 30,000 barrels per day were being produced in Ohio. The new field proved to be very extensive, and the Standard Oil Company bought property near Lima, Ohio, upon which they erected a large refinery. They disregarded the enormous difference in the sulphur content of Pennsylvania and Ohio oils, decided to refine the latter in the usual way and put it on the market. When the refined product had been distributed among their customers, it all came back as unfit for use. Every effort was made to solve the difficult problem, but in 1887, after two years of experimentation and with all the skill which the Standard Oil Company could call to their assistance, it was decided that no illuminating oil could be made from Ohio crude and that it was fit only for fuel. A pipe line for this purpose was built to Chicago, and long-term contracts made at 14 cents per barrel.

My patents had now been granted and I was selling refined Canadian oil with a guarantee that it would burn equal to the best Pennsylvania. After an investigation which convinced them that I had solved this problem, the Standard Oil Company bought my patents and my refinery, and as soon as possible Lima, Cleveland, Whiting, Philadelphia and Bayonne were refining oil by the new method.

The Ohio field was found to extend into Indiana and the production increased to 90,000 barrels per day. The price of this crude went up to nearly $1.00 per barrel, fluctuating between 60 cents and $1.00 for a great many years. The advantage resulting from the ability to use these oils for illuminants did not stop with the large profits of the Standard Oil Company, but the farmers and oil producers of Ohio and Indiana benefitted by the enormous advance in the value of Ohio crude, which amounted to many millions of dollars per year.

METHODS OF DESULPHURIZATION.

In desulphurizing petroleum, the oxide of copper is mixed with the petroleum distillate in a still supplied with an upright shaft and arms radiating therefrom, to keep the oxide in agitation during the process of distillation, flexible chains attached to the arms being used to prevent the copper from adhering to the bottom of the still. One hundred thousand pounds of oxide of copper are used for the first charge of 2,000 barrels of distillate. After 80 per cent. has been distilled off, a new charge of distillate is added with an additional charge of 30,000 pounds of copper, which is followed by two further runs, so that about 200,000 pounds of copper material are in the still when the fourth run is made. The residuum is pumped through a filter press, and the solid product of the filter press has the oil adhering thereto burned off. The dry mixture of oxide and sulphide of copper is

then put into a roasting furnace, where it is desulphurized to 1 per cent. or less.

A variation of my method treats the vapor coming from a still charged with crude petroleum, and consists in passing the vapor through two brushes made of No. 10 steel wire, the brushes being $5^1/_2$ feet in diameter and 16 feet long. They are inserted into a shell which is almost the same diameter as the brush, and the requisite amounts of copper and heavy oil are pumped into two shells, each containing one brush. The vapor passes in series, first around the shell to prevent condensation; then through the shells on to the condenser. The brushes are made to revolve at about six revolutions per minute. These wires immersing continually in this oxide of copper magma, the shells containing the brushes are surrounded by the vapor coming from the still, and as the temperatures of the vapors increase, anything condensed thereon during the prior period is reevaporated by the hotter vapor following.

Both these processes are now in operation at different works.

ROASTING FURNACE.

When the question of supplying the copper necessary for the works at Lima was under discussion, it was found that 160 furnaces, such as I used in Canada, would be required to do the work. In order to avoid the handling and transportation involved in such a gigantic furnace plant, I was obliged to construct a mechanical roasting furnace of a capacity in conformity with the magnitude of the business.

To eliminate the difficulties of the warping of the shaft and the arms which had caused the failure of the McDougal furnace, I constructed a stirring device, the shaft and arms of which were cooled artificially to withstand the high temperature of the roasting furnace. I first forced air as a cooling medium through the stirring device, but found that the oxidation of the sulphide of copper and the carbon from the residuum of the petroleum produced a temperature even higher than that of the ordinary pyrites furnace. It therefore became necessary to substitute hot water for air as a cooling medium, which proved very satisfactory. This made possible an increase in the size of the furnace to 16 feet inside diameter, and to-day these shafts and arms are connected with steam drums and are used like a water tube boiler, so that the surplus heat extracted from the stirring device of the roasting furnace is converted into steam and utilized in the plant. The capacity of a furnace is fifty tons per day, and four to six are used in one refinery. After the copper has been revivified, it is ground and mixed with residual oil from the filter press. In this manner the copper charge is pumped into the still which may be half a mile away. During the twenty years that this process has been in operation many millions of barrels of oil have been desulphurized.

CALIFORNIA OIL.

In 1902 the California field became important, and it was discovered that another oil which smoked chimneys had to be refined. This oil, however, was practically free from sulphur, the smoke being due to a large percentage of the aromatic series of hydrocarbons and to the fact that the percentage of hydrogen to carbon was too small to maintain the flame temperature necessary to consume all the carbon. I ascertained further that sulphuric anhydride converts the aromatic series into sulpho products, insoluble in petroleum, and that by treating the distillates from the crude oil with sulphuric anhydride, the members of the aromatic series in the petroleum can readily be extracted.

The existence of a petroleum containing nearly 50 per cent. of the coal-tar products is intensely interesting, especially in view of the theories advanced upon the origin of petroleum. The percentage of these hydrocarbons in the crude varies from the percentage contained in coal tar, benzol existing in a smaller proportion than toluol, while xylol represents 7 per cent. of the volume of the crude. Naphthalene, entirely free from all traces of carbolic odor, is quite prominent, while anthracene and carbolic acid are entirely absent.

I employed numerous methods for separating the products of California crude by physical means. Distillation, with large back-flow condensers attached, showed very encouraging results, as did also the method of washing the distillates with alcohol, carried on in series, the aromatic series being more soluble in alcohol than the paraffine series. However, the sulphuric anhydride treatment, which I first used in determining the amount of the two series contained in the petroleum, has proved to be very simple and effective on a large scale, and is now used by the Standard Oil Company at their plant in Port Richmond, California. The process of making the sulphuric anhydride employed there is the one purchased from the Verein Chemischer Fabriken of Mannheim. The capacity of the plant has been increased a number of times, until to-day it is by far the largest in the United States, if not in the world.

SULPHUR.

In 1865, while boring for petroleum in Louisiana, a sulphur deposit was discovered beneath a layer of quicksand about 500 feet thick. As a result of this discovery, quarrels and controversies arose as to whether the lease covering the petroleum rights also included the sulphur. It was some time before the matter was decided, and by the time a decision had been reached, both parties had lost a great deal of money, and those who got the sulphur deposit lost still more in trying to exploit it. The deposit seemed to bring misfortune to every one connected with it, and I have heard many stories and met many people who told me of having lost money in the various schemes that marked the progress of the sulphur mine. Progress there seemed to mean failure. An Austrian company, a French company, and numerous American companies—everybody failed and not a ton of sulphur was produced.

When I heard of this extraordinary situation, in 1891, I obtained a core from the sulphur deposit and

many pamphlets from the various companies who had tried to operate it, each one telling the prospective purchaser that his fortune was made if he but owned a few shares of the stock of that particular company. I became interested, and having had a great deal of experience in drilling and mining petroleum and salt, I thought the problem might be solved if all the facts concerning the deposit were known. Unfortunately, all the drilling records had been colored by the people who expected to float companies—everything unfavorable was concealed, and only that given which would be likely to induce investment, so that what I had considered a correct report proved later to be entirely wrong.

Being misinformed as to the character of the deposit, I reached the conclusion that the sulphur was distributed in the rock as in Sicily, and when I heard of the limestone roof covering the deposit, I felt that sulphur could be found anywhere within reasonable proximity to the sulphur mine.

To meet the extraordinary conditions existing in this deposit, I decided that the only way to mine this sulphur was to melt it in the ground and pump it to the surface in the form of a liquid. After careful study and consideration, I became convinced that this could be done. In view of the information obtained from the various companies, I believed that there was sulphur over miles of territory, and started to drill on land I had purchased within a mile and a half of Sulphur Mine. I went down over 2,000 feet without finding anything, then I located a second, a third, and a fourth well, but found no sulphur in any instance. This took much time and money, and I finally reached the conclusion that all the sulphur was located on the land owned by the New York company operating it at the time. They had a very ingenious scheme for sinking a shaft with a shield, but after the expenditure of a great deal of money, the shield was lost, and the danger due to the presence of water containing hydrogen sulphide was demonstrated by the death of a number of men. It was decided to abandon this method, especially after a drilling record had been made by a drilling company who reported direct to the owners, when it was discovered that there was no roof over the sulphur, and that sulphur water was permeating the deposit in inexhaustible quantities.

I realized at the outset that a method entirely different from that employed in the mines of Sicily was necessary for success here, as the class of labor required to operate this mine would demand at least $5.00 per day, while the Sicilian miners were being paid 60 cents.

I succeeded in getting possession of the property and at once set to work to drill a well of sufficient diameter to determine finally the character of the existing material. When this had been done, I was obliged to modify completely the process and apparatus I had expected to employ.

At that time the drilling of a well in an alluvial deposit containing quicksand, etc., was a very tedious task, and it took from six to nine months to get through the alluvial material to the rock—work which we do now in three days.

I drilled a well through the alluvial deposit to the rock with a 10″ pipe, then continued through the sulphur deposit, which was about 200 feet thick, with a 9″ drill, and immersed a 6″ pipe from the surface to the bottom in this well. The 6″ pipe had a strainer only 6″ long, at the very bottom, and a seat to receive the 3″ pipe through which we expected to lift the sulphur to the surface. The 6″ pipe, directly above the seat for the 3″ pipe, was also perforated for a distance of three feet.

After the well had been drilled and before the pipes were inserted, it was filled up with sand in order to insure a tight receptacle at the bottom for the liquid sulphur. After the sand had been washed out, the pipes were inserted and equipped, and the well was ready for the melting fluid.

This melting fluid consisted of water superheated to 335° Fahrenheit. The porosity of the rock in which the melting had to be done seemed to furnish an almost insurmountable obstacle to success, as I feared that the wild waters in the rock would break into the melting zone I expected to create and reduce the temperature of the fluid with which I expected to melt below the temperature necessary to fuse the sulphur. I had supplied a large number of boilers to furnish the heat necessary to maintain in the well a temperature higher than that required for the fusion of the sulphur.

The water was superheated in columns in which 100 pounds per square inch pressure was maintained, and the apparatus which I had constructed to accomplish this proved very efficient. We used twenty 150 h. p. boilers for a well, which represents experimentation on a ponderous scale.

When everything was ready to make the first trial, which would demonstrate either success or failure, we raised steam in the boilers, and sent the superheated water into the ground without a hitch. If for one instant the high temperature required should drop below the melting point of sulphur, it would mean failure, consequently intense interest centered in this first attempt.

After permitting the melting fluid to go into the ground for twenty-four hours, I decided that sufficient material must have been melted to produce some sulphur. The pumping engine was started on the sulphur line, and the increasing strain against the engine showed that work was being done. More and more slowly went the engine, more steam was supplied, until the man at the throttle sang out at the top of his voice, "She's pumping." A liquid appeared on the polished rod, and when I wiped it off I found my finger covered with sulphur. Within five minutes the receptacles under pressure were opened, and a beautiful stream of the golden fluid shot into the barrels we had ready to receive the product. After pumping for about fifteen minutes, the forty barrels we had supplied were seen to be inadequate. Quickly we threw up embankments and lined them with boards to receive the sulphur

that was gushing forth; and since that day no further attempt has been made to provide a vessel or a mold into which to put the sulphur.

When the sun went down we stopped the pump to hold the liquid sulphur below until we could prepare to receive more in the morning. The material on the ground had to be removed, and willing hands helped to make a clean slate for the next day. When everything had been finished, the sulphur all piled up in one heap, and the men had departed, I enjoyed all by myself this demonstration of success. I mounted the sulphur pile and seated myself on the very top. It pleased me to hear the slight noise caused by the contraction of the warm sulphur, which was like a greeting from below—proof that my object had been accomplished. Many days and many years intervened before financial success was assured, but the first step towards the ultimate goal had been achieved. We had melted the mineral in the ground and brought it to the surface as a liquid. We had demonstrated that it could be done.

This was especially gratifying as the criticisms I had received from technical papers and people who had heard of what I was attempting to do had been very adverse. Every one who expressed an opinion seemed to be convinced that this thing could not be done, one prominent man offering to eat every ounce of sulphur I ever pumped. A fair illustration of public opinion is the remark of the mail boy who drove me to the railroad the morning after our first pumping. He said: "Well, you pumped sulphur sure, but nobody believed it but the old carpenter, and they say he's half crazy."

This severe criticism, while not agreeable, did not carry very much weight with me. I felt that I had given the subject more thought than my critics, and I went about my work as best I could, thoroughly convinced that he who laughs last, laughs best.

At first we pumped with an ordinary deep-well oil pump, changed to meet the corrosive action of the sulphur. We experienced great difficulty with the valves in the pump, the high specific gravity of the sulphur, the great depth from which it had to be raised, and the corrosive action of the mineral itself making the maintenance of valves very difficult. Zinc and aluminum are practically the only two metals unaffected by liquid sulphur, but both these, being soft and easily disintegrated, would not withstand the shock at the change of stroke of the pump. I decided that if the specific gravity of the sulphur could be raised by the admixture of some other body much lighter, a point might be reached where the hydrostatic pressure of the water in the ground would raise the sulphur. Air seemed the most suitable, and we introduced compressed air into the column of liquid sulphur standing in the well, using a volume of two parts of air and one of sulphur. We have raised our sulphur discharge lines 70 feet above the ground, so that we can fill bins to a height of 65 feet without machinery or pump of any kind in the sulphur proper.

The first well lasted long enough to demonstrate the possibility of success, and to indicate in what directions improvements must be made. At that time, my sulphur enterprise was merely a hobby, the bulk of my time devoted to my Standard Oil work.

Many difficulties arose which we had not foreseen. We lost some wells because of the parting of the pipes. As the mineral was melted from the bottom, the earth above would follow as the sulphur rock settled. The grip of the sand and earth against the pipe was so great that instead of sliding, it would pull the pipe in two and the well would be lost. A 12″ pipe outside of the 10″, with stuffing box and telescope joints, obviated this difficulty. All wells, however, are eventually broken and crushed, when the abstraction of sulphur becomes so great that the cavity made cannot withstand the weight of the ground above it.

We succeeded in increasing the life of a well greatly by lining the hole drilled through the rock with a 9″ perforated pipe.

About that time we found that some wells gave out and ceased to pump when there had been no breaking of the pipes. I reached the conclusion that the cold sulphur water permeating the rock had broken into the melting zone, and brought the temperature of the melting water below the melting point of sulphur. I thought this might be remedied by pumping large amounts of a material like sawdust into the mine with the melting fluid, and that if the quantities of sawdust were large enough, the channels through which the wild waters in the rock entered the melting zone could be sealed.

One well, after pumping about 7,000 tons, at the rate of approximately 350 tons per day, ceased to produce. The pipes were all in good order, and we started to pump sawdust into the ground with the melting water. After pumping in about six carloads per day for five days, the well "sealed" with sawdust and promptly produced 39,000 tons more before the caving of the rock broke the pipes.

We perfected this method of artificially "sealing" the rock surrounding a melting zone, so that the amount now obtained from a well has been greatly increased. Whenever a well breaks, we shoot off with dynamite the 10″ pipe in the quicksand above the rock, and permit the sand to follow into the cavity from which the sulphur has been abstracted, filling up the space of the extracted sulphur rock with sand. The surface, consisting of about 200 feet of clay, follows the quicksand, gently but surely, and in order to maintain the pressure which is necessary to prevent the melting water from breaking into steam, the volume of the sulphur abstracted from below must be replaced by earth from above. To do this a dredge with a capacity of 4,000 cubic yards per day became necessary. Numerous reservoirs have been dug on the outskirts of the mine to supply the material required to do this. This filling has been going on constantly, and the ground has sunk to such an extent that where our house once stood is now 80 feet below the original surface.

These improvements were made slowly, as all experiments had to be made on a ponderous scale and

the smallest change required a great deal of time. During the long intervals which necessarily elapsed between my visits to the mine, I could give this new enterprise no attention. It took months to drill a new well when an old one was lost. At one time the work lay idle for a whole year before I could take it up again, and it was not until 1903 that we could see financial success ahead. In that year we produced 35,000 tons, and in 1904 enough to supply the entire consumption of the United States. It was in that year that we sent the first cargo of American sulphur to France.

In order to demonstrate what the mine could do with six wells, we pumped that number simultaneously for two months, producing 122,000 tons of sulphur, which is more than the consumption of the whole world for that period of time.

Prior to the development of the Louisiana sulphur mine, the sulphur production of the United States was less than one-half of one per cent. of its consumption, practically the entire amount required being supplied by Sicily and Japan. The former really had a monopoly of the sulphur business for a great many years. The Sicilian sulphur industry was closely interwoven with the politics of the islands, both internal and external. It was in 1833 that an English fleet appeared in the Bay of Naples to compel the Italians to rescind the sulphur monopoly that had been granted to France.

The ups and downs of the Sicilian sulphur business are extraordinary. The people, a large percentage of whom are employed in the mines, are very poor and used to be in the hands of dealers and usurers, who manipulated the sulphur market to suit themselves, and extremely high prices and extremely low prices followed each other as suited their convenience.

In England a process had been discovered for the recovery of sulphur from the waste products of the Leblanc soda process, quite a large amount of money being invested in the necessary machinery. When another sulphur crisis occurred in Sicily in 1894–5, and sulphur sold below the cost of production of English recovered sulphur, a number of English capitalists decided to finance and market the Sicilian output. They incorporated as "The Anglo-Sicilian Sulphur Company," and succeeded in getting between 75 and 85 per cent. of the Sicilian mine owners under contract for the entire output of their mines, whatever that might be, at a fixed price. This arrangement was made with the consent of the Italian Government for a term of five years, with the privilege of renewal for five years more. The scheme proved an excellent one, both for the Anglo-Sicilian Company and for the Sicilians. The former made a great deal of money, paying about 50 per cent. per annum on their common stock, and reserved large sums for contingencies. The contingencies arose in the form of the Louisiana sulphur production which came like a bolt out of a clear sky. They had received complaints from their agents here that the business in the west had diminished on account of sulphur furnished from a mine that was no mine at all, but where the sulphur came out of the ground ready to ship. The Anglo Company, as well as the Sicilians, declared that this was impossible, and that the whole thing was an "American swindle."

I was very anxious to get all the business possible, as our stock pile was much larger than our bank account, and I was surprised to hear that the Anglo-Sicilian Company had accepted a contract for 20,000 tons to be delivered in America, very much below the price they generally quoted, and not far above their cost. I decided to go to London and have a talk with them in order to find out if it would be necessary for us to put the price below their cost in order to maintain the American business which we needed very badly. I was perfectly frank and explained our position fully. I met with a great lack of enthusiasm for this "American humbug," and was told that they would go their own way, and I could go mine. I did. I had arranged for the sale of our sulphur in the various European countries, and knowing the production cost to my competitors, I succeeded very shortly in demonstrating that Louisiana sulphur was not a swindle. I found out afterwards that the lesson had cost the Anglo-Sicilian Company 285,000 pounds sterling—but then we were friends. Their attitude changed greatly, and they decided to go out of business and let the Sicilians and Americans take care of themselves.

The Anglo-Sicilian Company, especially during the last years of its life, had found it necessary to store a great deal of the sulphur tendered to them on their contracts, as they had lost the American market, which was their best customer, and it looked very much as though this enormous accumulation, approximating 500,000 tons, would have to be thrown on the market to be sold for whatever it would bring. To the poor Sicilian miner, whose lot under the most favorable circumstances is not an enviable one, this would have meant sulphur below cost, with the eventual closing of the Sicilian mines and misery and starvation to a large population.

The men well acquainted with the situation felt, as I did also, that this would result in revolution and bloodshed for Sicily. The laborers could not live on a wage lower than that which they already received. Frequent strikes and disturbances occurred when the misery of the working people was greater than usual.

Understanding the peculiar character of the Sicilians, the Government, when the matter was brought to their attention, decided to form an obligatory trust, so that no sulphur would be sold below cost, and the government was to finance the large stock on hand by issuing bonds and guaranteeing the interest. All the Sicilian sulphur mines were to be included in this obligatory trust, and the government agreed to advance, in cash, four-fifths of the value of the sulphur when it was received from the mine owners, the remainder to be paid to them after payment for the sulphur sold had been received and the expenses of conducting the business deducted.

A law creating this obligatory trust, which is known as the "*Consorzio Obbligatorio per l'Industrie Solfifera Siciliana*," was passed, and it has now been in operation since August 1, 1906. It has gone through the vicissitudes and occupies a unique position among the various trusts, which is of special interest to the United States. Here we have in successful operation a trust created by force, which all those engaged in that particular business are obliged to join. It has a board of thirty directors, an executive committee of ten, four of whom are members of the Government, and a Royal Commissioner, also appointed by the Government, who is practically its President. Prices are fixed and maintained, and sulphur is sold to all comers at the same figure.

This obligatory trust has been a godsend to the people, and so well are the Sicilians satisfied with its operation that they have already petitioned the Government to extend the period of its life beyond that originally decided upon. Moreover, the present Commissioner's able and wise administration has been so successful that the Sicilian stock of sulphur on hand and the obligation of the Consorzio towards the Government and the Bank of Sicily have been diminished to such an extent that the stock will be reduced to normal within two years and the Consorzio will be entirely out of debt. It is a striking illustration of the fact that a trust may be beneficial to all concerned. Great credit is due to the Italian Government for averting the misery which would inevitably have followed another sulphur crisis.

GEOLOGY OF THE SULPHUR AND SULPHUR OIL DEPOSITS OF THE COASTAL PLAIN.[1]

By Captain A. F Lucas.

In accepting the honor to make some remarks on the geology of the Great Calcasieu Sulphur Mines and the sulphur oil fields of the Coastal Plain, I have not done so because I consider myself a specialist, these subjects having been covered by far better pens than mine, but because the small part I played therein qualifies me in a small measure to join you in paying honor to a man who has through his ability, pluck and steadfastness attained international fame in solving a stupendous undertaking where many before him failed.

The geology of the sulphur mines and oil fields of the Coastal Plain is, of course, familiar to most of you, therefore I will only touch the subject by some practical observations, which through the success of Mr. Frasch have become of international importance and which makes me feel glad to be an American citizen.

America stands abroad as a great country and Americans as great men who do great things, men who, undaunted by failures of others, have undertaken and carried to practical solution problems that appeared foolhardy to undertake, and the success of this accomplishment must in all candor be ascribed to genius, especially so when this genius compels other nations to take notice and "willy-nilly" pay him tribute.

The geology of the Coastal Plain—which of course includes the mounds or domes—extends over a vast area, practically beginning at the northwestern coast of Florida for about 50–100 miles in width, and following the littoral zone of the Gulf States of Alabama, Mississippi, Louisiana and Texas down to Mexico and beyond.

This vast area is practically as level as a floor, with a slight dip toward the sea, and in traveling westward one comes upon slight elevations of say from 10-100 feet in height over the surrounding prairie. These elevations, which we will later on feel warranted in calling domes, are of limited area, say from 250–2,000 acres which have by now assumed wonderful economic importance.

It is, therefore, precisely of these elevations that we will speak, for they now form the basis of the whole economic geology of the Coastal Plain in the states of Louisiana, Texas and the Gulf States of Mexico.

To attempt to make soundings in search of minerals of economic value beyond this elevated zone is perfectly useless as the drill will only encounter the clays, sands and gravel of the Pleistocene Columbia series, then the red sands of the Neocene Lafayette series and deeper down the blue clays, "Gumbo" and sporadic laminations of limestone, at which time the driller (if he is lucky to have reached this depth safely) will be glad to pull out and call it done.

It is true, however, that at times these elevations are so slight that the "wild catter" often confuses them with the local phenomena of the ant mounds and feels warranted to drill anyway, and we have instances on record where he eventually hit the apex of a hidden dome as it happened for instance at Batsom Prairie, Texas, whereby he obtained economic results.

Undoubtedly there are more such hidden domes scattered over this vast area, and I make a passing reference to the possibility of their existence in order to point out the hazard of hitting any, as very great.

We will now proceed from New Orleans westward and come upon "Belle Isle," the first of a series known as the five Salt Islands.

They are called in sequence "Belle Isle," "Cote Blanche," "Grand Cote," "Petite Anse" and "Jefferson Island." The last named was the winter home of the late Joe Jefferson, the actor.

These Islands are of limited area, or from 250–1200 acres in extent and rise abruptly out of the surrounding marshes at an elevation of from 60 to 200 feet. They have all been explored and salt found thereon except "Cote Blanche."

On Belle Isle salt was found at 101 feet in depth and the drill continued in salt to the depth of 3,250 feet. Unfortunately, owing to its hardness at the bottom, it has been impossible to obtain drilling to

[1] Address delivered at the Perkin Medal Meeting, Society of Chemical Industry, Chemists' Club, Jan. 19, 1912.

classify the geological age upon which this enormous salt dome rests.

Salt at Grand Cote was found at 102 feet and at 900 feet the drill stopped in salt.

At Petite Anse salt was discovered at 15 feet depth while digging a water well, and subsequent drill tests made failed to pass through salt at 1500 feet.

At Jefferson Island, the shallowest soundings where salt was found was 91 feet from the surface and the drill stopped, still in salt, at 2,090 feet.

The salt of all these domes is of remarkable purity, 98–99 per cent. sodium chloride, except perhaps at Belle Isle where part of this salt mass is saturated with petroleum. Following the contour of this dome by drilling near the apex and while sinking a shaft the occurrence of Galena and Sphalerite was ascertained. The crystals are all sharp, and show no sign of erosion. Dr. A. C. Gill, of Cornell University, states that the Galena shows no silver and the probability is that it represents a deposition from salt water by chemical action.

The borings made at Belle Isle for oil and sulphur have disclosed lenses of considerable limestone and sulphur and pools of water escaping from some wells are strongly charged with H_2S and SO_2, and yet the oil recovered from these wells gives no indication of containing sulphur in any form. This oil is paraffine base, of 45° B., and has the appearance of Pennsylvania crude only somewhat lighter in color. Upon submitting a sample of this oil to the Standard Oil Company officials it was difficult to convince them that this oil had not already been refined in whole or in part.

Further explorations on this island have been suspended, as it was found unpractical to work the same for oil or salt. Grand Cote and Petite Anse are now producing a superior quality of rock salt, most of which is shipped to the northwest in competition with the Michigan and New York salt.

Anse La Butte, six miles north of Lafayette, is also a salt dome of limited area which, however, has so far produced a few good oil wells. The oil carries some sulphur and is of 21° B. and is used principally for fuel.

The Jennings field on which oil was found at 1800 feet in considerable quantities is also a dome, but so far no salt has been found thereon. It is believed by Professor G. D. Harris, of Cornell University, who for many years has carried on most thorough and indefatigable work on the Coastal Plain of Texas and Louisiana, that larger oil resources lie beyond the limit of the proven field.

Of smaller importance is the field of Welsh, which is producing, however, an excellent grade of oil, but so far no salt-rock has been found, and the wells as a rule yield the best result at about 1,000 feet. This field gives no indication on the surface of primary or secondary doming.

The oozing of petroleum and escape of gas at Bayou Choupique, now known as the sulphur mines, led the Louisiana Oil Company to drill for oil in 1865, and after going through the clays and sands of the Pleistocene, the quicksands and gravels of the Columbia to 443 feet, entered a gray massive limestone of about 60 feet in thickness. Under this, almost pure alternate layers of sulphur and limestone were found for a thickness of about 260 feet; below this lies the gypsum beds with occasional layers of pure sulphur. It remains to be proved by deeper drilling if this dome is also underlayed by rock salt. The geological age of this dome has been ascribed by Hilgard as Cretaceous, by Harris as Eocene. The fossils as classified by Van Ingen are of Tertiary and by Dall and Aldrich, of Miocene origin.

A new company was organized by General Jules Brody to win this sulphur by sinking an iron ringed shaft, and after reaching a depth of 110 feet the shaft was abandoned on account of a break in the lining and the asphyxiating of several miners by sulphur gas.

Mr. Frasch became interested in this sulphur deposit about 1893 and at once proceeded to experiment on practical and scientific lines, to-wit, by "the Frasch hot water fusing process." Sulphur is known to fuse at about 114° C., and he undertook to fuse this sulphur mass by injecting superheated water directly in contact with the sulphur deposit below, raising the fused sulphur by specially constructed pumps. Later on he improved this method by forcing the fused sulphur out of a concentric pipe by means of compressing hot air through a central pipe. This method proved a technical success at the start, but it required a genius to overcome the immeasurable difficulties to bring it to a commercial success such as it has been now for a number of years. Any one will agree with me if he were to see a number of pipes, of say 3 or 4 inches in diameter, perched about 40 or 45 feet in height, ejecting pure liquid sulphur at the rate of 500 tons per day into enormous bins. As the sulphur cools, it solidifies quickly, so that one can see a block of sulphur grow in a few days to a great cube of about 200 by 300 feet and 60 feet high, which block may contain over 100,000 tons of pure sulphur of commerce.

Since the advent of the sulphur no serious attempt has been made to explore the sources of heavy oil that still flows from the upper layers of some old test wells except by the Beaumont boomers in 1901, and I am of the opinion that if Mr. Frasch were to make a serious attempt he would succeed not only in getting the oil in gushers, but also little Chinamen with fire-crackers from the lower regions.

Numerous attempts have been made to explore the "Vinton Dome" about fifteen miles west of Sulphur, but progress was impeded principally owing to the heavy gravel and quicksand beds of the Columbia, until about one year ago the many efforts have been crowned with success. The Vinton field now furnishes considerable oil of about 21° B. which carries about half per cent. sulphur.

You have all heard from the fields of "Spindle Top," "Sour Lake," "Saratoga," "Humble," etc. They are also salt domes and have produced great quantities of sulphur oil of an average specific gravity

of 22° B. Spindle Top alone is credited with about forty three million barrels of oil to date.

On Spindle Top was made the first discovery of sulphur oil of the Coastal Plain on January 10, 1901. It is also a salt dome and lies at an elevation of only 12 feet from the surrounding prairie, the surface of which contains about 235 acres only. Explorations had been made in 1882, 1885 and 1888 in search of sulphur or oil, but owing to alternating beds of quicksand and gravel of the Columbia, it was found impossible to go deeper than 300 feet, until in October, 1900, I made the second attempt, and after going through irregular alternating beds of clays, sand, gravel, lime, calcite and sulphur, reached the oil rock at 1120 feet depth. The pressure of gas and oil was so great that the four-inch drill pipe was shot out to a great height, carrying the head block, swivel and cable with it. Then a great rush of mud and water came out (the water used for drilling) followed by the ejection of large fragments of dolomite and fossils. It settled then to a steady flow of oil to a height of about 200 feet through a six-inch pipe. The well flowed continuously for ten days when it was finally closed by an eight-inch gate valve. This oil was heavily saturated with H_2S and SO_2 and was very offensive to the nose while the well was in eruption, as within a radius of several miles all houses painted with white lead were blackened, also the silver in houses and even to the silver coins in circulation. It was estimated that this well flowed in ten days while in eruption about 750,000 barrels of oil. The oil rock is a porous dolomite carrying some sulphur in crystals and containing considerable calcium or magnesium.

The size of the cavities in the dolomite can be estimated only by the large fragments shot out from the wells while in eruption. Drillers, however, reported instances of their tools dropping for several feet leading one to conclude that the oil rock is cavernous, which in consequence made an admirable storage reservoir for the oil. The actual thickness of the oil-bearing rock is undetermined, but it has been estimated to be from 75–150 feet thick. A test well drilled near the discovery well entered gypsum at about 1200 feet and at 1650 feet encountered rock salt which continued to a depth of 1900 feet when drilling stopped.

The discovery of this oil pool started a celebrated boom in Texas and Louisiana. Many men and women with speculative oil tendencies were stirred up from Mexico to the Appalachians with Spindle Top as an objective centre. The mere fact of land being in the vicinity of Beaumont sold it at fabulous prices, while fractions of an acre on Spindle Top sold at the rate of $760,000.00 per acre. Not that there was any value thereon warranting such prices, but that it enabled the boomer to capitalize his twenty-five by thirty feet of land, near a known gusher, at millions of dollars. However, by the time he was through with the sale of his stock, widely advertised, a well came in dry and the boom collapsed, and so did most of the many hundreds of companies capitalized at enormous figures. Had Spindle Top been sanely exploited by experienced drillers, I am confident that it would gush to-day.

Still traveling westward we come upon other domes such as "Hoskins," "Bryan Heights," "Big Hill in Matagorda" and "Big Hill in Jefferson County," "Damon," "Kyser," "High Island," "Barber Hill," etc., all of which have been explored but so far have been found barren in whole or in part.

High Island and Damon Mound, two interesting elevations of 50–100 feet above the surrounding prairies, and of about 3,000 acres in extent each, have practically the same characteristic indications that Spindle Top had, to-wit: the elevation above the prairie indicating a possible dome, the sour water, the springs charged with the hydrogen sulphide, the gas escape, etc. The opening of a well, drilled by hand at High Island in search of water, was plugged with straw and a few years later the plug was extracted and found to be a solid mass of sulphur, yet after repeated drilling to a considerable depth on this island and Damon Mound nothing of commercial importance was found. The drill passed through alternate beds of quicksand, silicious clay, sulphur and clay, some oil and rock salt at bottom.

At Big Hill, Jefferson County, Texas, also an attractive possibility for an oil proposition, solid dolomite was found at 350 feet, which continued to a depth of 1400 feet when drilling was discontinued.

At Bryan Height a great gas pressure was encountered in 1901 charged with hydrogen sulphide, but it was subsequently abandoned. Big Hill, Matagorda County, had a small production. The oil was found at depths of 885–1050 feet, in limestone which possesses the same characteristic features of the oil-bearing rock of Spindle Top. As much as 60 feet of solid sulphur was reported from some wells, and always near the oil horizon. The oil was proportionately charged with it and the gas, chiefly H_2S mixed with SO_2.

In conclusion I would say that the domes of the Coastal Plain have broken the world's precedents: First, for the limited area; second, for the productiveness as yet developed, and this holds good for sulphur, oil and rock salt, which goes to the credit of the Coastal Plain only.

There are other richly productive fields of somewhat older geology, but want of time precludes me from describing them.

By glancing at the map you will note that the Southern Pacific Railroad found itself to be located onto every field as fast as discovered, and I was told by a "wag" that when the Almighty created the Universe He also located this railroad, and at once got busy to provide material for this road to haul, and that is the reason *why* He *placed the sulphur deposit* and oil pools and the rock salt adjacent to its line. This road was the first one to utilize this cheap and convenient resource as fuel and this at a minimum cost.

He then improved and grew magnificent forests

of timber also adjacent to this line, and prepared the soil for the unexcelled culture of rice and sugar.

The whole of these enormous commercial resources were placed by Him so to speak in the front yard of this fortunate railroad and without the expenditure of a dollar for their advertising bureau, so that I feel justified, in concluding, to call the foregoing "The Economic Geology of the Southern Pacific Railroad."

SULPHUR MINES OF THE UNION SULPHUR COMPANY IN LOUISIANA.[1]

By F H. Pough.

Mr. Frasch has given us a most interesting description of the discovery and development of Sulphur Mine and of the Frasch Process, but for which this enormous deposit of sulphur would to-day be absolutely worthless. Much that he has told us was quite new to me and so little has been published heretofore about these deposits which was authentic, that I think we are all to be congratulated upon hearing at first hand so much of the inside history of the development of this, the largest sulphur mine in the world.

[1] Lecture illustrated by lantern slides and moving pictures, delivered at the Perkin Medal Meeting, Society Chemical Industry, Chemists' Club, Jan. 19, 1912.

After what Mr. Frasch has told us there is really nothing more to be said in further description of the process, but if you will allow me, I will try to give you some further details as to the size of the deposit, the output and the method of storing, handling and shipping our product. After having done this, as it is customary to chaperon visitors to the mine, it will be my pleasant duty to conduct you over the mine as I cannot actually take you through it in the conventional way, the Frasch method of operating making the mine too damp and warm for comfort. I shall endeavor to do this with the aid of about thirty lantern slides and some motion pictures.

I think I should add that the motion pictures[1] were made during the past week, especially for presentation before you this evening so that practically you will see the work going on as it was at the mine to-day. As a matter of fact the undeveloped films did not reach New York until Wednesday and I saw the finished films for the first time late this afternoon.

Fig. 1.—Employees' Dwellings at Sulphur Mine.

Sulphur Mine is located about three miles from Sulphur, Calcasieu Parish, Louisiana, a town of about 1,000 inhabitants on the Southern Pacific. From

[1] List of titles of motion pictures of Union Sulphur Co. Mine shown by Mr. Pough: Entrance to Mine; Panorama of Works from Office; Scenes from Belt Line Train, Sulphur Wells and Derricks; Filling Bins with Liquid Sulphur; Blasting Sulphur; Men Working in Sulphur; Loading Sulphur in Box Cars; Loading Sulphur in Open Cars; Dredge in Operation; Men Going Home from Work; and Panoramic View of Workmen's Homes.

600–700 men are regularly employed at the mine, so that you will see it is quite a community of itself, and every effort is made by the Company to further the comfort of the men. A complete sewerage system has been established and the Company owns a number of houses, which it rents to the older employees, the foremen and members of the office force at a nominal rental. It is compelled as a matter of public necessity to operate a boarding-house for the unmarried men, but as this results in a yearly loss to the Company of from $8,000 to $10,000, it is hardly a paying enterprise. Mr. Frasch is so set against anything that might be looked upon as an exploitation of the men or that might lead to it, that not only is no company store or anything of that nature permitted, but no private commercial enterprise of any kind is allowed upon or near the Company's property, unless a barber shop can be so classed.

The sulphur deposit, as shown by test borings, is quite sharply defined and nearly circular in shape. It is considerably more than half a mile in diameter,

FIG. 2.—A WELL DISCHARGING 500 TONS OF MOLTEN SULPHUR PER DAY.

and I can assure you that you will find your trip this evening much more comfortable than had you made it with me on foot last July, although as the mine is encircled by a standard gauge railroad some three miles in length, we could have placed an engine and a flat car at your disposal. While we claim to be up-to-date in all other respects, we have to confess

that our passenger accommodations on the railroad are somewhat primitive.

The sulphur apparently was deposited in the cone of a great geyser, which dates back to the tertiary period, and is contained in a limestone formation in the proportion of about 70 per cent. sulphur to 30 per cent. limestone. The sulphur beds, which are underlain by a bed of gypsum, extend to a depth of 1100 feet or more.

When you visit the mine, the most conspicuous objects, next to the well derricks which dot the landscape in great profusion, are the boiler stacks, of which there are over 130, each stack representing a boiler of 150–300 h. p. These boilers are arranged in eight batteries, containing with one exception 15 or 20 boilers each, and each battery is capable of operating a well. As a rule two batteries are placed in a group so that one foreman can oversee both. The boilers are fired entirely with fuel oil and but three men, two firemen and one water tender, are required on each shift to attend to the firing, and the feed water in each battery. The total boiler capacity is in the neighborhood of 25,000 h. p. and you will therefore see that there is installed at Sulphur Mine one of the largest industrial steam generating plants in the world, a unique feature of which is the fact that an almost negligible quantity of the steam generated is used for power.

In a building to the rear of each battery are located the pumps and superheaters. The latter are vertical, cylindrical receptacles, about 4 ft. in diameter by 16 ft. high, containing a series of shallow trays over which water pours and is thus brought into intimate contact with live steam from the boilers. The problem of heating the great quantity of water required for the operation of the wells to the proper temperature was a difficult one and the method described is another of Mr. Frasch's ingenious inventions. Possibly a better idea of the capacity of this plant can be gained from the fact that the consumption of fuel oil amounts to 700 barrels per day at each battery, when operating at full capacity; that the average total daily consumption of water is about 7,000,000 gallons, and the average yearly consumption of fuel oil over 1,000,000 barrels.

FIG. 3.—100,000-TON BLOCK OF SULPHUR.

The enormous amount of water required for the boilers and superheaters is provided for by means of a pumping station located on the Houston River, about 6 miles from the mine. This pumping station contains a centrifugal pump having a capacity of 12,000,000 gallons per day and the water is carried to the mine by means of a private canal. To sup-

plement the pumping station and provide against breakdowns, there is an artificial storage reservoir, covering 150 acres.

The wells are sunk in groups, the individual wells being placed 50 100 feet apart, and one well will sometimes produce as high as 400 500 tons of sulphur per day, and keep up a steady flow for months at a time—in one case the output from a single well reached 73,000 tons. I might say here that one of our wells is now producing considerably more than 500 tons a day and has been for some weeks. The average output is over 250,000 tons per year but the only limitation is the market demand.

daily. As the bed of sulphur grows in thickness, the sides of the bins are raised by means of additional uprights and planking until they reach a height of 60 ft. or more. When a bin is filled, another is built alongside of it, as shown in the pictures, so that in this way (Fig. 2) continuous blocks of sulphur may be formed several hundred feet in length by 150 feet or more in width, and, as I have said, 60–65 feet in height. Blocks of sulphur have thus been formed containing as much as 150,000 tons.

When it is desired to ship the sulphur, a movable track is laid as a spur from the main line, parallel to the long side of the bin. The boards from this

FIG. 4.—LOADING 35 TONS OF SULPHUR IN 14 MINUTES.

The liquid sulphur as it flows from the wells is so pure that we are able to guarantee a sulphur content of 99½ per cent., for as a matter of fact the average purity is well above that figure. The sulphur is collected and stored in large bins about 150 by 250 ft. square, which are made by setting posts into the ground to which are nailed 2″ × 12″ planks of suitable length. The sulphur is delivered into the center of these bins and caused to spread in thin layers about 1″ thick, which cool so rapidly as to permit continuous operation. A separate bin is used for each well in order to permit accurate measurement of the output which is carefully taken and recorded

side are then removed and the sulphur thrown down by means of blasts placed near the bottom of the pile. The sulphur is then picked up and loaded into cars by means of locomotive cranes fitted with grab buckets capable of handling 2 tons at a time and of loading a 35-ton car in 14 minutes. Shipments from the mine have frequently reached 1,000 tons per day for periods of 20–30 consecutive days.

A large quantity of sulphur is shipped directly from the mine in closed cars which are loaded by box car loaders, but by far the largest portion of the sulphur is shipped by rail in open, bottom-dump cars to Sabine, Texas, in trains of about 20 cars,

where it is loaded into steamers for distribution along the Atlantic Coast and for export to Europe.

The loading plant at Sabine has a capacity of from 600–800 tons per hour, and the facilities are such that it is possible for a 7500-ton steamer to dock, load and sail within 12 hours. It is customary for the steamers to come to the dock with the hatch covers raised, and while I was at Sabine last January I saw our own steamer, the "HERMAN FRASCH" begin to load sulphur within 15 minutes from the time she was made fast to the dock. The "HERMAN FRASCH," I might say incidentally, was built for us at the Quincy yards of the Fore River Shipbuilding Company and launched in December, 1909. She has a cargo-carrying capacity of 5500 tons and we are now contemplating building a second ship of somewhat smaller capacity. In addition to our own steamer we usually have two or three steamers under charter.

The sulphur is handled at Sabine by means of cranes and grab buckets similar to these used at the mine, which deliver the sulphur into hoppers, from which it falls upon a rapidly moving system of belts, which carry it to the dock and up an incline to a height of about 10 feet above the steamer's deck. From the inclined belt it falls into an adjustable iron chute in the form of a pipe which telescopes, from which it drops into the hold of the steamer. By turning this iron chute from side to side, it is practical to load the cargo so evenly that no trimming is required in our own steamer, or vessel designed for carrying bulk cargoes.

SCIENTIFIC SOCIETIES

FORTY-FIFTH ANNUAL MEETING A. C. S. PROGRAM OF PAPERS.

At the forty-fifth meeting of the American Chemical Society, held in Washington, December 27–30th, a large number of important and instructive papers were presented under the various divisional heads. The following program indicates the character of material discussed. The greater portion of these papers will appear in the Journals of the Society.

DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS.

G. D. ROSENGARTEN, *Chairman.*
F. E. GALLAGHER, *Secretary.*

Relation of Ultimate Composition to Calorific Power in Coal. By H. C. SHERMAN, D. A. BARTLETT AND N. E. WEATHERLESS.

Relation of Proximate Composition to Calorific Power in Coal. (Preliminary Report). By H. C. SHERMAN AND S. H. REGESTER.

Preliminary Note of the Production of Mercury Fulminate. By CHARLES E. MUNROE.

The Present Status of the Gas Industry and its Outlook. By CHARLES E. MUNROE.

New Forms of Gas Analysis Apparatus. By G. A. BURRELL.

New Forms of Apparatus for Gas Analysis. By F. M. WILLIAMS.

Problems in the Manufacture of C. P. Acids. By J. T. BAKER.

A Rapid Method for the Determination of Vanadium in Steels, Ores, etc., Based on its Quantitative Inclusion by the Phosphomolybdate Precipitate. By J. R. CAIN AND J. C. HOSTETTER.

Valuation of Fluorspar. By ERNST BIDTEL.

The Quality of Commercial Kerosene. By L. B. LOCKHART.

Notes on a New Type of Extraction Thimble. By P. A. BOECK.

The Effect of Filtration upon the Physical Properties of Petroleum Oils. By J. P. SIMMONS AND O. J. STEEPLE, JR.

The Direct Determination of Small Amounts of Platinum in Ores and Bullion. By F. P. DEWEY.

The Product Patent. By F. P. SUMMERS.

The Use of Potassium Cyanide Solution in the Investigation of the Structure and Conductivity of Copper, Copper-covered Steel and Other Metals. By J. O. HANDY.

An Apparatus and Improved Method for Determining Quantitatively Hydrogen Sulfide in Illuminating Gas. By E. P. HARDING AND E. JOHNSON.

Free Lime in Portland Cement. By H. E. KIEFER.

Glass Analysis. By W. C. TAYLOR AND E. C. SULLIVAN.

The Estimation of Absorbed Gases and Oxygen in Copper by Ignition in Carbon Dioxide and Hydrogen. By G. L. HEATH.

Symposium on Mineral Wastes.

Informal discussions of losses in the preparation and utilization of mineral products, and of wastes, inefficient methods and proposed improvements of processes in the chemical technology of mineral substances.

Carbon Waste. By J. A. HOLMES.

(*a*) Zinc Losses in Brass Manufacture. (*b*) Need of Special Alloys for Special Uses. By W. H. BASSETT.

Losses of Combined Nitrogen. By J. D. PENNOCK.

New Uses to Reduce Abuses in Conservation. By W. R. WHITNEY.

Wastes in the Ceramic Industry. By A. V. BLEININGER.

The Abuse of Brand. By A. D. LITTLE.

Waste and Conservation of Potash and Phosphoric Acid. By F. K. CAMERON.

Sulfur Fumes and Flue Dust. By F. G. COTTRELL.

Miscellaneous Mineral Wastes. By CHARLES L. PARSONS.

DIVISION OF AGRICULTURAL AND FOOD CHEMISTRY.

H. E. BARNARD, *Chairman.*
B. E. CURRY, *Secretary.*

A Study of the Pollution of the Ohio River Bordering Indiana. By H. E. BARNARD, Chairman's Address.

A Modification of the Tiemann-Schulz Method. By W. A. WITHERS AND F. W. SHERWOOD.

Determination of Small Amounts of Caffeine—A Comparison of Methods. By B. L. MURRAY.

The Filtration of Soil Solutions. A New Filter for this and Similar Purposes. By W. H. ROSS AND R. C. BENNER.

The Presence of Lead and Copper in Cream of Tartar and Tartaric Acid. Technical Methods to Purify These Products. By FERNAND BRUNSCHWIG.

The Forms of Phosphorus in Cotton Seed Meal. By J. B. RATHER.

An Electric Conductivity Test for Purity of Maple Syrup. By J. F. SNELL.

A Brief Study of the Phosphorus of the Matière Noire. By JOHN STEWART.

The Composition of Free Oyster Liquid. By EMMA CRANDAL.

New Data on the Composition of Prepared Mustards. By H. E. BISHOP.

A Method for the Separation of the Seven Coal Tar Colors when Occurring in Mixtures. By J. M. PRICE.
Altering the Composition of Indian Corn by Seed Selection. By L. H. SMITH.
Influence of Reaction of Culture Medium on Root Development of Wheat Seedlings. By J. F. BREAZEALE AND J. A. LECLERC.
The Study of True and Imitation Graham Flour. By J. A. LECLERC AND B. R. JACOBS.
The Desiccation of Potatoes and the Uses of the Product. By C. C. MOORE.
Marking of Porcelain and Silica Crucibles, etc. By P. A. YODER.
Perilla Oil. By CHARLES FOX.
Bacterial Activities in Frozen Soils. By P. E. BROWN AND R. E. SMITH.
Report of Progress in a Study of the Maine Sardine Industry. By H. H. HANSON.
The Index of Refraction of the Mixed Acids of Fatty Oils. By W. B. SMITH.
The Profitable Application of Chemistry to the Milling Industry. By B. H. KEPNER.

DIVISION OF PHARMACEUTICAL CHEMISTRY.

B. L. MURRAY, *Chairman.*
F. R. ELDRED, *Secretary.*

Our Advances and Retrogressions in Pharmaceutical Chemistry. By B. L. MURRAY, Chairman's address.
Smoking Opium: Its Manufacture and Chemical Composition. Exhibit-Samples and Smoking Outfit. By A. B. ADAMS AND J. M. DORMAN.
An Improved Method of Assay for Aromatic Sulfuric Acid. By LINWOOD A. BROWN.
The Pharmacopoeial Requirements for Cannabis Sativa. By H. C. HAMILTON.
Notes on Cannabis Indica. By H. C. HAMILTON.
Progress on the Work of Revision of the United States Pharmacopoeia. By JOSEPH P. REMINGTON.
The Estimation of Morphine in Cough Syrups. By A. D. THORBURN.
Laboratory Studies of Rennin. By A. ZIMMERMAN.
The Bromine and Iodometric Methods for the Volumetric Estimation of Cresol. By C. M. PENCE.
The Analysis of a Very Old Sample of Powdered Gelsemium Root. By L. E. SAYRE.
A Bromine-Hydrobromic Acid Method for the Determination of Phenols. By ATHERTON SEIDELL.
Impurities of Anesthetic Chloroform and their Detection. By CHARLES BASKERVILLE AND W. A. HAMOR.
The Influence of Patents and Trademarks on the United States Pharmacopoeia. By M. I. WILBERT.
The Estimation of Morphine in Pills, Tablets, Etc. By J. B. WILLIAMS.
Notes on Mastic and Sandarac. By FRANK O. TAYLOR.
The Alcohol Requirement of the Pure Food and Drug Law and the Accuracy of Alcohol Assays of Pharmaceutical Preparations. By C. H. BRIGGS.
A Laboratory Study of Vegetable and Mineral Oils. By FRED KLEIN.
Comments on Tests of the U. S. Pharmacopoeia, Eighth Revision. By FREDERICK J. AUSTIN.
Suggested Modifications to the U. S. P. Assay of Opium. By R. NORRIS SHREVE.
Some Unfamiliar Facts about Familiar Detergents. By F. P. DUNNINGTON.
Colocynth U. S. P. By J. R. RIPPETOE AND R. MINOR.
Estimation of Antipyrine in Acetanilid or Acetphenetid in Mixtures. By W. O. EMERY.
Estimation of Codein in Acetanilid or Acetphenetidin Mixtures. By W. O. EMERY.
Standard for Tincture of Ginger. By L. F. KEBLER.
Estimating Small Quantities of Morphin in Mixtures. By E. O. EATON.
Estimating Small Amounts of Nitroglycerin. By A. G. MURRAY
Standards and Methods. By L. F. KEBLER.

DIVISION OF FERTILIZER CHEMISTRY.

PAUL RUDNICK, *Chairman.*
J. E. BRECKENRIDGE, *Secretary.*

Fertilizer Chemistry—A Report of Progress. By PAUL RUDNICK, Chairman's Address.
The Effect of the "Wet Process" on the Availability of Low-Grade Nitrogenous Materials. By B. L. HARTWELL AND F. R. PEMBER.
A Method for Testing Out Problems in Acid Phosphate Manufacture. By F. B. PORTER.
Exact Work in Fertilizer Analysis. By I. K. PHELPS.
Activity of Organic Nitrogen as Measured by the Alkaline Permanganate Method. By C. H. JONES.
Fertilizer Economics. By H. G. BELL
The Sulfur Requirements of Crops in Relation to the Soil and Air Supply. By E. B. HART.
Note on the Permanganate Methods for Availability of Organic Nitrogen. By J. P. STREET.
Conductivity Method of Making Neutral Ammonium Citrate Solution. By A. J. PATTEN.
Committee Reports.

SECTION OF INDIA RUBBER CHEMISTRY.

D. A. CUTLER, *Chairman.*
F. J. MAYWALD, *Secretary.*

Scientific Tests in Methods for Rubber Content in Raw and Vulcanized Rubber. By W. A. DUCCA.
On Mineral Compounds Used in Rubber. By S. P. THACHER.
A Few Notes on Rubber Goods Used in Beet Sugar Factories. By VICTOR HANZLIK.
The Treatment of Crude Rubbers. By F. R. PEABODY.
Does the Acidity of Crude Rubber Indicate its Botanical Origin? By DAVID BLOOM.
Apocynum Rubber. By CHARLES FOX.
Report of Committee on Rubber Analysis. By CHARLES KNIGHT.
Discussion on:
Synthetic Rubber.
Effects of Oils and Other Adulterants in Reclaiming Rubber.
Uses of Ceylon Rubbers.

MINUTES OF DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS.[1]

The Industrial Division met at the McKinley Manual Training School, Washington, D. C., December 28, 29 and 30, 1911, with the chairman, George D. Rosengarten, presiding.

The Chairman reported for the Executive Committee that the Divisional Committees on Official Specifications and on Standard Methods of Technical Analysis were to be combined into one committee of five members, to be called Committee on Standard Specifications and Methods of Analysis; that a scheme presented by the Secretary for the guidance of the committees of the Division was adopted; that the Committee on Definition of Trade Terms

[1] Forty-fifth meeting, American Chemical Society, Washington, December, 1911.

was to be continued for one year; and that the financial report of the Secretary was approved. On vote, this report was accepted by the Division.

The report of the Secretary was read and accepted upon the vote of the Division. This described the publication of circular letters, the by-laws and the directory of the Division, and reported upon its present financial condition.

Miscellaneous expenditures	$ 30.98
Printing of Directory (approx.)	100.00
Mailing of Directory	22.00
Total expenditures	$152.98
Cash received from dues	65.00
Deficit—December 26, 1911	$87.98

A motion of T. J. Parker, seconded by W. R. Whitney, was passed, instructing the Secretary to send bills to members for the Divisional dues, these bills to be marked "Voluntary Contribution."

Informal reports were received from the committees on—

Analysis of Soap Products and Glycerine, Research Problems, Standard Methods of Technical Analysis.

Reports were presented by the committees on—

Definition of Trade Terms, Official Specifications, Special Compounds, and Professional Code of Ethics.

A proposal was made by Percy H. Walker that when the Division votes upon the acceptance of specifications proposed by the Committee on Standard Specifications and Methods of Analysis, the right of suffrage be limited to representatives of consumers. After a spirited discussion, a motion by G. E. Barton was passed "that the vote on acceptance of specifications be limited neither to producers nor to consumers."

The Nominating Committee, consisting of W. R. Whitney, T. J. Parker and Percy H. Walker, reported on the officers for 1912, who were duly elected.

Chairman, GEORGE D. ROSENGARTEN.
Vice-Chairman, GEORGE P. ADAMSON.
Secretary, FRANCIS E. GALLAGHER.
Executive Committee:

OFFICERS,
M. C. WHITAKER, *Ex officio*,
W. H. WALKER,
S. W. PARR,
ARTHUR LOWENSTEIN,
W. D. RICHARDSON,
H. S. MINER.

Program of papers listed elsewhere in this issue.

It was voted, on the motion of R. M. Shreve, that the paper by Mr. Summers, entitled "The Product Patent," be referred to the American Chemical Society Committee on Patent and Related Legislation (Charles E. Munroe, chairman) for consideration. This committee is now considering patent legislation.

One entire day was devoted to a very successful symposium on "Mineral Wastes and Conservation" under the leadership of Charles L. Parsons. A stenographic record of the papers and discussion will be published in the March issue of THIS JOURNAL.

At the conclusion of the symposium, the appreciation of the Division was voted to Professor Parsons for arranging and conducting this very attractive feature. F. E. GALLAGHER, *Secretary*.

MINUTES OF DIVISION OF AGRICULTURE AND FOOD CHEMISTRY.[1]

Meeting was called to order by Mr. H. E. Barnard, Chairman of the Division. The following papers were read:

H. E. Barnard. Chairman's Address. "A Study of the Pollution of the Ohio River Bordering Indiana."

W. A. Withers and F. W. Sherwood. "A Modification of the Tiemann-Schulze Method."

B. L. Murray. "Determination of Small Amounts of Caffeine —A Comparison of Methods."

W. H. Ross and Raymond C. Benner. "The Filtration of Soil Solutions. A New Filter for This and Similar Purposes."

J. F. Snell. "An Electric Conductivity Test for Purity of Maple Syrup."

Emma Crandal. "The Composition of Free Oyster Liquid."

H. E. Bishop. "New Data on the Composition of Prepared Mustards."

J. M. Price. "A Method for the Separation of the Seven Coal Tar Colors when Occurring in Mixtures."

J. A. Le Clerc and B. R. Jacobs. "The Study of True and Imitation Graham Flour."

C. C. Moore. "The Desiccation of Potatoes and the Uses of the Product."

P. A. Yoder. "Marking of Porcelain and Silica Crucibles, etc."

P. E. Brown and R. E. Smith. "Bacterial Activities in Frozen Soils."

H. H. Hanson. "Report of Progress in a Study of the Maine Sardine Industry."

The Executive Committee of the Division presented the following Tentative By-Laws to govern its meeting, which matter had been referred to this committee by the Division at the Indianapolis meeting.

Tentative By-Laws for the Division of Agriculture and Food Chemistry.

Article 1.—Membership.

Membership of the Division shall be open to all members of the American Chemical Society and any member of the Society shall upon request to the Secretary of the Division be registered as a member of the Division.

Article 2.—Officers and Manner of Election.

1. The Officers of the Division shall be a Chairman, a Vice-Chairman, a Recording Secretary and an Executive Committee. The Chairman, Vice-Chairman and Recording Secretary shall be members of the Executive Committee, *ex-officio*.

2. The Chairman of the Division shall be Chairman of the Executive Committee.

3. The Executive Committee shall consist of two members of the Division and the members, *ex-officio*, provided by Section 1 of this article.

4. The Chairman at the first session of the Division shall appoint a committee of three who shall present nominees for the offices. The officers shall be elected annually by ballot at the last session of the Division held during the annual meeting of the Society, and shall take office at the close of the meeting at which they are elected. They shall hold office for one year

[1] Forty-fifth General Meeting American Chemical Society, Washington, December, 1911

or until their successors are elected. Officers may be reelected, but, with the exception of the Secretary, shall not serve in any one office more than two consecutive years.

5. The Executive Committee shall fill any vacancies that may occur among the Officers of the Division

Article 3.—Duties of Officers.

1. It shall be the duty of the Chairman to represent the Division in the Council of the Society, to preside at meetings of the Executive Committee, to carry into effect the decisions and recommendations of that committee, to prepare a program for the general meeting, to preside at State Meetings of the Division and to deliver an address to the Division at its general meetings.

2. In absence of the Chairman, the Vice-Chairman or Secretary at any stated meeting their places shall be filled temporarily by the Executive Committee.

3. It shall be the duty of the Recording Secretary to keep a record of the proceedings of the Division and of the Executive Committee, to maintain a list of members, to send to members such notices as the business of the Division may require, to transmit to the Secretary of the Society the names of all officers and standing committees of the Division within ten days of their appointment; and in like manner to notify the Secretary of the Society of any changes of Officers or standing committee during the year.

4. The Recording Secretary shall be the custodian of the records, communications, documents, and papers of the Division. He shall have charge of the funds of the Division and shall make all disbursements, subject to the authorization of the Executive Committee. He shall report to the Division at its general meetings.

5. The Executive Committee shall conduct the business of the Division and direct its activities. At each general meeting of the Society the Committee shall, as early as possible, hold a meeting to consider the affairs of the Division and receive reports of its committee. The Executive Committee, exclusive of the Secretary, shall be responsible for all expenditures not authorized by the Council, and shall audit the accounts of the Secretary previous to the annual meeting.

Article 4.—Meetings.

1. There shall be a meeting of the Division at each general meeting of the Society. Business effecting the organization (Amendments, elections of officers, etc.) of the Division shall be transacted only at meetings coincident with the annual meeting of the Society.

2. The order of business shall be as follows:

(*a*) Reading of the Minutes. (*b*) Reports of the Chairman and Secretary. (*c*) Reports of the Executive Committee. (*d*) Reports of Committees. (*e*) At the annual meeting, election of officers. (*f*) Reading of Papers and Discussions. (*g*) Miscellaneous Business.

The regular order of business may be suspended at any session by the consent of three-fourths of the members of the Division present.

Article 5.—Special and Standing Committees.

The Chairman shall appoint, from time to time, committees of the Division to consider, conduct and report upon such special matter as may be delegated to them.

Article 6.—Expenses.

The Executive Committee may make an annual assessment of not to exceed 50 cents per member, to meet the expenses of the Division, including non-serial publications.

Article 7.—Amendments.

These By-Laws may be amended at any annual meeting of the Division by a three-fifths vote of the members present, provided notice of the proposed amendment together with the text thereof has been sent to each member of the Division at least two weeks before the annual meeting. Amendments, to be effective, must be approved by the Council and accepted by that body as not inconsistent with the Constitution and By-Laws of the Society.

These By-Laws presented were discussed at some length by the members of the Division present and were finally adopted as tentative, in order to govern the meeting, with the exception of Article 6 which relates to the annual assessment.

It was decided to publish these By-Laws and bring them up for final action before the Division at the next meeting.

Following officers were elected for the ensuing year.

Chairman, H. E. Barnard; *Vice-Chairman*, E. W. Robison; *Secretary*, G. F. Mason; *Executive Committee*, C. D. Wood, H. S. Bailey, W. M. Allen.

G. F. MASON, *Secretary.*

MINUTES OF THE DIVISION OF PHARMACUETICAL CHEMISTRY.[1]

FIRST SESSION.

The first session was called to order by the chairman, B. L. Murray, at 10.00 A.M., December 27th, at the McKinley High School, twenty-two members present.

The Secretary reported an increase in membership from seventy at the beginning of the year to one hundred and sixty-four at the present time; and, as treasurer, reported total receipts of $75.00, total expenditures of $61.35, and a balance of $14.15.

Dr. L. F. Kebler presented a report for the Executive Committee and expressed his satisfaction at the progress of the division.

The report of the Committee on Quantitative Methods was read by the Secretary in the absence of the chairman of the committee, F. O. Taylor. The report was formally accepted, and a motion prevailed authorizing Mr. Taylor to publish a bibliography on the quantitative estimation of mercury compiled by the committee.

The chairman of the Committee on Quantitative Methods was authorized to use his discretion in the selection of work for the coming year, and the executive committee was empowered to make such changes in the organization and size of the former committee as seemed best.

The first paper, on "Smoking Opium: Its Manufacture and Chemical Compositions," by A. B. Adams and J. M. Doran, was read by Mr. Adams, who exhibited a complete smoking outfit and a considerable number of samples of smoking opium. Mr. Doran contributed some interesting facts in regard to the traffic in smoking opium.

Dr. Caspari, Jr., recommended the discontinuance of aqueous solid extracts of opium and prohibition of the sale of preparations of opium below the United States Pharmacopoeial standard of strength.

It was pointed out that the aqueous extract had already been withdrawn by most of the pharmaceutical manufacturers, but L. F. Kebler expressed the opinion that this would not remedy the evil, as habitues would still obtain opium in some form; and that the only remedy was the complete government control of the sale of opium and its preparation.

Messrs. Adams and Doran were given a vote of thanks for presenting the exhibit in connection with their paper.

Mr. L. A. Brown presented a paper on "An Improved Method of Assay for Aromatic Sulphuric Acid," which was discussed by several members, and it was suggested that, as the present U. S. P. method had been shown to be inaccurate, it should be replaced by some method such as that proposed by Brown.

"Progress on the Work of Revision of the United States

[1] Forty-fifth General Meeting of the American Chemical Society, Washington, December, 1911.

Pharmacopoeia" was presented by Jos. P. Remington and was followed by a general discussion of matters pertaining to the pharmacopoeia.

SECOND SESSION.

W. O. Emery presented two papers entitled, "Estimation of Antipyrine in Acetanilid or Acetphenetidin Mixtures" and "Estimation of Codeine in Acetanilid or Acetphenetidin Mixtures."

F. P. Dunnington presented a paper on "Some Unfamiliar Facts about Familiar Detergents."

R. Norris Shreve read a paper on "Suggested Modifications of the U. S. P. Assay of Opium."

M. I. Wilbert discussed "The Influence of Patents and Trade Marks on the United States Pharmacopoeia," and L. F. Kebler presented, in abstract, a paper by E. O. Eaton, on "Estimating Small Quantities of Morphine in Mixtures."

A. G. Murray presented a paper on "Estimating Small Quantities of Nitrogen."

Other papers on the program whose authors were not present were read either in full or in abstract by the secretary.

THIRD SESSION.

Chairman B. L. Murray presented his annual address on "Our Advances and Retrogressions in Pharmaceutical Chemistry," and a committee consisting of Chas. Caspari, Jr., M. I. Wilbert and R. Norris Shreve was appointed by the acting chairman to report on recommendations contained therein.

L. F. Kebler then presented two papers on "Standard for Tincture of Ginger" and "Standards and Methods."

A. Seidell presented a paper on "A Bromine-Hydrobromic Acid Method for the Determination of Phenols." These papers were discussed collectively, followed by a general discussion of drug assaying and pharmacopoeial standards and tests.

FOURTH SESSION.

The following resolutions were passed:

Resolved, "That the Division of Pharmaceutical Chemistry of the American Chemical Society respectfully urge the United States Pharmacopoeial Revision Committee to change the present form of stating solubility data from the parts of solvent to dissolve unit quantity of substances, to the grams weight of substances which are dissolved per 100 grams of the saturated solution."

On motion this resolution was referred to the Committee on Revision of the U. S. Pharmacopoeia.

Resolved, "That the Division of Pharmaceutical Chemistry of the American Chemical Society recommend to the Committee of Revision of the United States Pharmacopoeia (IX) the retention of the form and style of spelling the names of the substances now used in the Eighth Revision, and that the official names of the new substances to be admitted be brief and distinctive."

Resolved, "That it is the sense of the members of the Division of Pharmaceutical Chemistry of the American Chemical Society present, that in stating the strengths of acids in the U. S. P. they be stated in such terms as hydrogen chloride, HCl ('absolute hydrochloric acid')."

The chairman then called L. F. Kebler to the chair and Chas. Caspari, Jr., presented the report of the committee on the chairman's address, favoring the suggestion made by the chairman and recommending that a committee of three, including the chairman of the Division, be appointed to confer with the president or other suitable officers of the Society in regard to the connection which the Division should have with the publication of pharmaceutical literature in the Society's journals. This report was adopted.

The chairman took the chair and the following resolutions introduced by M. I. Wilbert were passed and referred to the Society's Committee on Patents.

Resolved, "That the members of the Division of Pharmaceutical Chemistry of the American Chemical Society favor amending the present patent laws so as to provide adequate protection for the original invention of a useful article or process for making the same."

Resolved "That we depreciate the issuing of product patents for substances of a chemical nature."

Resolved "That we favor a literal interpretation of the present Trade Mark Registration law so that names used solely as generic titles for widely used substances will become public property on the expiration of the period for which they are registered."

The following resolution introduced by F. R. Eldred was passed and referred to the Bureau of Standards.

Resolved "That, as the members of the Division of Pharmaceutical Chemistry feel the need of accurate tables giving the refractive indices of mixtures of alcohol and water and having the same range as the specific gravity tables for alcohol, we suggest that the Bureau of Standards should consider the preparation of such tables."

The election of officers for the ensuing year resulted as follows:

Chairman, B. L. Murray; *Vice-Chairman*, L. A. Brown; *Secretary*, Frank R. Eldred; *Members of Executive Committee*, L. F. Kebler, Atherton Seidell.

The Division adjourned *sine die*.

FRANK R. ELDRED, *Secy.*

MINUTES OF THE MEETING OF THE FERTILIZER DIVISION.[1]

Meeting called to order December 28th by Chairman Mr. Paul Rudnick.

The following papers were presented:

Paul Rudnick. Address. "Fertilizer Chemistry, a Report of Progress."

Burt L. Hartwell and F. R. Pember. "The Effect of the 'Wet Process' on the Availability of Low-Grade Nitrogenous Material."

F. B. Porter. "A Method for Testing Out Problems in Acid Phosphate Manufacture."

I. K. Phelps. "Exact Work in Fertilizer Analysis."

C. H. Jones. "Activity of Organic Nitrogen as Measured by the Alkaline Permanganate Method."

H. G. Bell. "Fertilizer Economics."

E. B. Hart. "The Sulfur Requirements of Crops in Relation to the Soil and Air Supply."

John Phillips Street. "Note on the Permanganate Methods for Availability of Organic Nitrogen."

A. J. Patten. "Conductivity Method of Making Neutral Ammonium Citrate Solution."

There was much interest and discussion on the papers relating to Availability of Organic Nitrogen and Neutral Ammonium Citrate.

The following Committee reports were given:

Committee on Nitrogen; Committee on Potash; Committee on Phosphate Rock; Committee on Fertilizer Legislation.

Officers were elected for 1912:

Chairman, Paul Rudnick; *Vice-Chairman*, J. P. Street. *Secretary*, J. E. Breckenridge; *Executive Committee*, F. B. Carpenter, A. Lowenstein, W. J. Jones, Jr., and G. Farnham.

J. E. BRECKENRIDGE, *Secretary*.

[1] Forty-fifth General Meeting American Chemical Society, Washington, December, 1911.

MINUTES OF THE MEETING OF THE RUBBER SECTION.[1]

December 29. The morning session was opened with 37 members present, and 17 came in during the session.

The following program was presented:

"Scientific Tests and Methods for Rubber Content in Raw and Vulcanized Rubber," by W. C. Ducca. Discussion by Messrs. Boggs, Cutler and others.

"The Treatment of Crude Rubber," by Mr. Peabody. Discussion at some length by Messrs. Whipple, Barrier, and Boggs.

"Rubber Goods Required in Beet Sugar Factories," by Mr. Hanslick.

"A Punching Machine for Rubber Samples," by H. P. Mills.

Dr. Leo Backeland announced the joint meeting to be held during the summer of 1912, in conjunction with the Section of Plastics of the International Congress of Applied Chemistry.

The secretary announced that the former chairman of the Section, Mr. Goodrich, had donated $100 to the funds of the Section, and that the present chairman, Mr. Cutler, and also Mr. Harold Van der Linde had agreed each to donate the same amount.

Dr. Knight, Chairman of the Committee on Standard Methods of Analysis, reported for that committee, and submitted such figures as had been received by him. The report was discussed by Messrs. Wesson, Boggs, Walker, Hibbert, and Cottle.

It was then voted that the report of the Committee on Methods be accepted, and that the committee be discharged with thanks.

"Does the Acidity of Rubber Indicate its Botanical Origin?" by Mr. Bloom, was read, and discussed by Messrs. Evans, Boggs, and Maywald.

The chairman called up for discussion the subject of Synthetic Rubber and made a lengthy report as to work which had been done on the investigation of synthetic rubber by the Rubber Goods Manufacturing Company. He stated, among other things, that the synthetic rubber made by his company from isoprene obtained from turpentine could not be vulcanized by itself, but that vulcanization did take place if any other rubber was added to the synthetic rubber. He said further, however, that synthetic rubber made from isoprene obtained from Cameroon rubber could be readily vulcanized. He also stated that his Company had been investigating the subject of synthetic rubber for the past ten months, and that with isoprene at 50 cents a pound, the price at which they had obtained it, the price of the resulting synthetic rubber would be thoroughly satisfactory. The matter was discussed by Messrs. Boggs, Maywald, and others.

Mr. Barrows gave a short talk on his theory of the formation of the rubber molecule. This theory was discussed at length by Mr. L. G. Wesson and others.

The chairman called for discussion on the effects of oils and other adulterants in reclaiming rubber. Discussion by Messrs. Whipple, Cutler, Boggs, and Boughton.

In the absence of Mr. Thacher's paper on "Mineral Compounds Used in Rubber," the question of the use of sublimed white lead in rubber compounds and its exclusion from such compounds by various specification was brought up by Mr. Boggs, and discussed by Messrs. Whipple, Barrier, Walker, Tuttle, Hanslick and Wesson.

December 30th. The meeting was called to order at 9.50 by the chairman, with 37 members and visitors present. The meeting was first addressed by Mr. Parsons, Secretary of the Society.

Officers were elected for the ensuing year: Mr. Cutler, Chairman; Mr. Whipple, Secretary.

There was then a general discussion on the appointment of a Committee on Standardizing Methods of Rubber Analysis, by Messrs. Walker, Fay, Geer, Culter, Boggs, and Parsons. It was voted that a committee of five, consisting of the chairman, secretary, and three of the members, elected by ballot, appoint a Committee on Standard Methods of Analysis. Messrs. Geer, Boggs, and Fay were duly elected to serve with the Chairman and Secretary, and on motion this Committee was made the Executive Committee for the ensuing year.

Mr. Walker, on behalf of the Bureau of Chemistry, and Mr. Smith, on behalf of the Bureau of Standards, offered the facilities of their respective bureaus to the committee. Mr. Geer announced informally that his Company was prepared to detail some of its chemists to carry on work for the committee.

It was unanimously voted that every member of this Section would coöperate with the Committee on Methods of Analysis.

A vote of thanks was extended to Mr. Goodrich, the former chairman, for the work which he had done during his administration.

The question of abstracts in the Abstract Journal was discussed by Mr. Evans, Mr. Barrier, and others. The secretary read a letter which he had received from Mr. Whittelsey in reply to criticisms which had been made as to rubber abstracts in the Journal.

Dr. Gray announced that he had found isoprene present in certain crude petroleums, but would not state in what particular petroleums he had found them.

The following new members joined the Section:

I. V. Stone, Revere Rubber Co., Providence, R. I.
John A. Schaeffer, Picher Lead Co., Joplin, Mo.
F. E. Barrows, Patent Attorney, 918 F St., Washington, D. C.
H. B. Rodman, Pennsylvania Railroad, Altoona, Pa.
E. W. Boughton, Bureau of Chemistry, Washington, D. C.
Norman G. Madge, Chief Chemist, Continental Rubber Co. of N. Y., 11 Vandewater St., New York, N. Y.
John B. Tuttle, Bureau of Standards, Washington, D. C.
William H. Smith, Bureau of Standards, Washington, D. C.
D. Whipple, 114 Liberty St., New York, N. Y.
Percy H. Walker, Bureau of Chemistry, Washington, D. C.
Henry Fay, Massachusetts Institute of Technology, Boston.
Joseph Westesson, Navy Yard, Washington, D. C.
Laurence G. Wesson, Bureau of Standards, Washington, D. C.

F. J. MAYWALD, *Secretary.*

NOTES AND CORRESPONDENCE

NOTE ON THE PRODUCTION OF MERCURY FULMINATE.

By CHARLES E. MUNROE.

Although it is stated that mercuric fulminate has been produced through the reaction taking place between sodium nitromethane and mercuric chloride, yet, since the discovery of mercury fulminate by Edward Howard in 1800, it has been commercially produced through the reactions occurring between ethyl alcohol, mercuric nitrate and nitric acid or its derivatives. In 1888 I began, in a desultory way, the study of this reaction when other alcohols were substituted for ethyl alcohol and, though methyl alcohol failed to give any satisfactory results, it was found that propyl, butyl, amyl and the higher alcohols gave bodies allied to fulminic acid but containing a larger number of carbon atoms or alkyl groups.

A closer study of these reactions and particularly the ob-

[1] Forty-fifth Meeting, American Chemical Society, Washington, December, 1911.

served fact that the reaction between ethyl alcohol and mercuric nitrate, even when well acidified with nitric acid, did not proceed, except when nitrogen oxides were present, or until they had been formed, suggested that the first step in the reaction consisted in the conversion of the alcohols into aldehydes, and that then and only then were the fulminates formed. This suggested the substitution of aldehydes for alcohols and on using them, beginning with acetaldehyde, as the parent substances it was found that not only were fulminic acid and substituted fulminic acids produced but that the reactions ran on much more smoothly and completely.

As I have said these operations were conducted in a desultory way and continued over a term of many years, for my duties have been numerous and exacting and they have continually encroached on my efforts to conduct researches. Fortunately I have now an accomplished student, trained in this field, who appreciates the problem and has entered on its solution and I hope soon that we may present a fuller statement and a more complete record of these interesting reactions and the results that follow from them.

GEORGE WASHINGTON UNIVERSITY,
December, 1911.

TUNGSTEN PRODUCTION IN THE UNITED STATES IN 1911.

There was a sharp falling off in the production of tungsten ores in 1911, owing to the decrease in the market for tool steels, in which the bulk of the tungsten is used. According to preliminary figures collected by Frank L. Hess, of the United States Geological Survey, about 1,125 short tons of concentrates carrying 60 per cent. tungsten trioxide were produced and shipped during the year, which is less than two-thirds of the output for 1910, when 1,821 tons were marketed. The prices for the year ranged from $4.50 to $8.50 per unit, depending on quantity, quality, and individual bargaining. At the close of the year $5.00 per unit was offered. The unit is twenty pounds of tungsten trioxide per short ton of ore.

As usual the Boulder County (Colorado) field gave the largest returns, 740 tons, and the Atolia (California) deposits the second largest. Smaller amounts were produced in Arizona, Nevada, Idaho, and Washington.

The ore mined in Boulder County is ferberite (iron tungstate), which is not obtained in large quantity at any other place in the world. In spite of the poor market several new companies were formed to mine ore in the Boulder field and commenced operations during the year. Two companies profitably worked over tailings left from former operations. A considerable quantity of the ore mined both in this and in other fields was not marketed.

The Atolia field did not make so large a production as in 1910, but carried on work through most of the year.

Near Nipton, Cal., work was done by several persons on tungsten-bearing veins, but most of the ore was left at the mines to await higher prices.

In Arizona a number of carloads of ore were mined near Arivaca, more than 70 miles south of Tucson, and hauled to that place for shipment to Denver for milling.

The tungsten ore in the Blue Wing district had been long mistaken for a dark zinc blende, with which it occurs.

New discoveries of wolframite were reported from the vicinity of Oroville, Wash., and in silver-bearing veins in the Sonoma Range, south of Golconda, Nev., Hünberite was found in veins once worked for silver in the Potosi district, 9 miles from Pony, Mont., and scheelite was found in gold veins in the New Goldfield district near Rebel Creek, Nev.

CLAY PRODUCTS IN 1910.

The products of the clay-working industries in the United States—brick, tile, pottery, etc.—reached in 1910 the largest value ever attained, the total being $170,115,974, compared with $166,321,213 in 1909. These figures are presented by Jefferson Middleton, of the United States Geological Survey, in an advance chapter from "Mineral Resources" for 1910—"Clay-Working Industries."

In the brick and tile industry building brick of all kinds except fancy or ornamental declined in value, while drain tile, sewer pipe, architectural terra cotta, fireproofing, stove lining, and fire-brick showed gains. In the pottery industry every item increased in 1910 except stoneware and yellow and Rockingham ware, which showed a loss of about $200,000.

The following are the ten States with highest recorded production for 1910:

State.	Brick and tile.	Pottery.
Ohio	$17,231,236	$14,294,712
Pennsylvania	19,814,355	2,279,930
New Jersey	9,245,854	8,588,455
Illinois	14,331,414	844,747
New York	9,778,288	2,093,661
Indiana	7,143,306	956,704
Missouri	7,058,705	29,061
Iowa	5,310,706	17,535
California	4,744,968	97,423
West Virginia	1,322,457	2,675,588

LEAD INDUSTRY IN 1910.

According to a report by C. E. Siebenthal just issued by the United States Geological Survey the total production of primary lead from all sources, domestic and foreign, made a gain of 5 per cent. over that of 1909. Missouri made individually a larger gain than the whole domestic increase and produced over 43 per cent. of the domestic output of lead. The total production of refined lead in this country in 1910 was 470,380 short tons, the greatest output in the history of the industry.

The total quantity of primary lead produced in Missouri in 1910 was 161,659 short tons, Idaho was next with 99,924 short tons, Utah third with 57,081 short tons, and Colorado fourth with 35,685 short tons.

THE WORLD'S PRODUCTION OF LEAD, 1910, IN SHORT TONS

Australia	108,907
Austria-Hungary	19,290
Belgium	43,651
Canada	16,535
France	23,148
Germany	174,053
Great Britain	33,620
Greece	18,519
Italy	17,639
Japan	3,858
Mexico	138,890
Russia	1,323
Spain	211,201
Sweden	331
Turkey in Asia	13,999
Other countries	14,220
United States (domestic)	372,227
Total	1,211,411

CONSULAR AND TRADE NOTES

GERMAN POTASH INTERESTS.

Consul George Nicolas Ifft, Nuremberg, reports that the announcement of the discovery of potash in the United States always attracts much attention in Germany, and a recent announcement of this sort brought forth a statement from the German Potash Syndicate that it had at once caused inquiry to be made by an expert official and found that the efforts of both the United States Geological Survey and the Department of Agriculture have thus far failed to locate any valuable potash beds. The newspaper report was declared to have been based on the well-known but unimportant potash beds in Death Valley. The Potash Syndicate puts little faith in the production of potash from the kelp of the Pacific coast, declaring that its production, except as a by-product of iodine, would not pay.

The general press was not so skeptical, however, and referred to the news as at least a warning that Germany's natural monopoly in the potash field is not so certain for the future as has been supposed, and that it must so organize itself as to be ever ready to meet new competition.

NORWEGIAN GUANO SHIPMENTS TO UNITED STATES.

Consul P. Emerson Taylor, Stavanger, reports that the largest shipment of fish guano and whale meal ever made from this district to the United States went from this city to Charleston, S. C., on November 25, 1911. The shipment aggregated 20,179 bags of 100 kilos each, or a total of 4,439,380 pounds, invoiced at $95,769. The shipment consisted of 12,981 bags (2,855,820 pounds) of herring guano, priced at $65,802, 6,682 bags (1,470,040 pounds) of whale guano, priced at $27,197, and 516 bags of whale-meat meal (113,520 pounds), priced at $2,769.

A tramp steamer was chartered by the seller and manufacturer of the guano and whale meal and the shipment was made direct from this port to Charleston, the product being sold to a New York firm. The total export of fish guano and whale meal from this district to the United States in November, 1911, aggregated $105,407.

GLASS PAVING BLOCKS IN FRANCE.

Consul Carl Bailey Hurst, Lyon, has investigated the supposed use of glass bricks or blocks manufactured for pavements, with the following result:

Seven or eight years ago a plant was established at La Demi Lune, a suburb about 4 miles from Lyon, for making glass paving material under the name of "pierre de verre Garchey." After many experiments carried out at the factory the manufacturer applied to the Lyon municipality for the right to make a trial on one of the chief thoroughfares. The necessary authorization was granted, provided that the inventor would bear the entire expense of the undertaking. The place chosen for laying the glass pavement was a section of the Place de la République, where traffic of cabs, automobiles, and wagons of all kinds is very heavy. The glass bricks remained in place for less than two years, and were then taken out, as they were in very poor condition; the edges were all broken, and in many cases the blocks were split through and through.

The opinion of officials here at that time was to the effect that this glass pavement could be used under favorable circumstances for sidewalks, but not for the middle of streets.

The manufacturer after the failure of his experiment closed or dismantled his small factory, left Lyon, and his address is not ascertainable. At present only stone and wood are employed for pavements in this city.

PALM-OIL INDUSTRY OF WEST AFRICA.

Consul William J. Yerby, Sierra Leone, gives an interesting report on the palm-oil industry of West Africa. The amount of palm oil annually exported from British West Africa now amounts to 15,150,000 imperial gallons, valued at not less than $5,750,000, while the yearly export of palm kernels is 226,000 long tons, valued at over $16,000,000. These figures do not include the exports of palm oil or kernels from French West Africa, German West Africa, nor the Kongo. The palm tree from which the oil and kernels are obtained is indigenous and grows in great quantities in all West Africa. It is most prolific from the Cameroons to and including a part of French Guinea, the area embracing Northern and Southern Nigeria, the Gold Coast, the Ivory Coast, Dahomey, Togoland, the Kongo, Liberia, and Sierra Leone.

The trees are 30–40 feet high, and bear as many as 7 or 8 cones of fruit each about the size of a man's head. These cones are studded with the kernels, which consist of the fibrous outer coating or pericarp, which contains the palm oil and the oil and the palm nut, enclosed in a thin shell. The pericarp and the kernel yield about 60 and 50 per cent., respectively, of their weight in oil. The oil obtained from the pericarp is a deep yellowish blood-red, while that from the kernel is white. Both the palm oil and the palm-nut oil are used locally instead of lard. The natives and some Europeans claim that it has a fine flavor.

There is no cultivation of the fruit other than gathering it when matured. The kernels are prepared by beating the fruit in a mortar until the pericarp is separated from the enshelled kernel. The emulsified pericarp is then boiled in water in a large pot, that part of the oil that has not already been freed collecting at the top. The kernels are cracked one at a time with a hammer or stone by the women and children. There are now on the market several machines for removing the pericarp and cracking the kernels, but they have not as yet proved a success.

The only drawback to the wide-spread development of the palm-oil industry in West Africa is the lack of transportation, and this will not be overcome until the country is well opened up. Steady progress is being made in this direction, however. There are large palm-bearing districts not far from the coast and on the verge of wide navigable rivers, where the question of transportation involves no great difficulty or expense, and it is in these districts that the industry will first be undertaken on a large scale. As plam oil will bring $150 per ton in Europe at the present time, and as, handled on a large scale, it could be delivered in Liverpool for $75 per ton, including all charges with the cost of production, it can be easily seen that future developments will be rapid and have an important bearing on the general prospects of West Africa. The amount of trade here is doubling every 10 years, and promises in the near future to rival that of South Africa.

INCREASED CUSTOMS DUTIES IN BOLIVIA.

Just prior to the adjournment of the Congress of Bolivia, in November, 1911, the duties on all foreign products were increased 15 per cent. and a duty of 2 per cent. was imposed on all foreign products hitherto free of duty under the tariff. These new tariff rates take effect January 1, 1912.

BOOK REVIEWS

Addresses to Engineering Students. Edited by WADDELL AND HARRINGTON, Consulting Engineers, Kansas City, Missouri. First Edition 1911. 480 pages. Price: $1.00 for single copies obtained from the editors; 75 cents when distributed in quantities to Universities and Colleges.

The object of the Editors, as stated in the preface, is to acquaint students with the importance of the engineering profession and of its ethics. They also draw attention to the generally recognized shortcomings in English, especially that relating to engineering in most of the courses covering that subject. It is recommended by the editors that the book be used as a text-book or one of reference.

It is rather a shock to one's sense of ethics to find an address verging closely on the line of exploitation and the qualification may be superfluous, placed beside the addresses of Dr. Eliot, Prof. Karapetoff and others especially when it is recommended by the editors that this compilation of addresses be used as a text-book to help mold and guide the prospective engineer in the "ethics of his profession."

The first address, quite properly, is "Advice to Freshmen." It is by Dean Shenehon. It contains considerable wise counsel but we regret to observe the rather "flippant" way in which he treats a pecuniary obligation. The attitude which some people assume when a money obligation is involved is strange and unfortunate. Dean Shenehon would have his students believe, if only by inference, that it is rather "smart" to play "fast and loose" with a money obligation. The existing condition is bad enough and we can not look for much improvement so long as such doctrine is preached to students. Fortunately, subsequent addresses in the compilation remove the sting of this shortcoming in Dean Shenehon's remarks.

The second address is by Prof. J. B. Johnson on "Two Kinds of Education for Engineers." He states: "Engineering differs from all other learned professions, however, in this, that its learning has to do only with the inanimate world, the world of dead matter and force. The materials, the laws and the forces of nature, and scarcely to any extent its life, are the peculiar field of the engineer." And further: "In short what interest is there for him (the Engineer) in what we now commonly include in the term humanities." This to us seems just the contrary to the policy which is being evolved by the best minds in charge of our engineering courses. The situation is different from that which existed a generation or more ago, and the contrast is becoming more pronounced as our industrial development proceeds. It was not long ago when courses in civil engineering predominated but to-day the field for mechanical and electrical engineer is in the ascendance and, relatively speaking, civil engineering is of minor importance. While we admit that ethics do not change, we must insist there are other things that do and one of these is the field of the engineer during the material progress of a country.

Now, educating students along exclusively highly technical lines, somewhat as Prof. Johnson outlines, has created a certain degree of prejudice against the technical graduate because the line of training has not complied to the conditions to be met. It has resulted principally through the neglect of that very element which Prof. Johnson says does not concern the engineer.

The material progress of any country consists largely in the construction and consequent operation of industrial establishments. Their operation is more or less perpetual. To successfully conduct the affairs of these establishments is the province of the engineer and requires:

1st. An engineering knowledge.

2nd. The ability to successfully handle human nature—the ability to obtain the highest initiative of each individual. This is a widely varying quantity but one which is largely controlled by a few underlying principles.

The first qualification without the second will almost always spell failure. The second with even only a smattering of the first will generally bring success but the combination of the two indicates the broadest type of engineering. Many an establishment has been doubled in capacity when the only variable was the one in charge of the operation and when both men may have been equals in technical knowledge. We do not mean to say there is no field for the highly educated technical engineer. There is such a field and it is a vast one but the field for the operating engineer is increasing at a very rapid pace and the training which is necessary for its fulfilment is not met by our present engineering courses. The student should be taught that knowledge is not judgment, that success or failure is measured by results and that an idea without the ability to execute is, to that extent, worthless. If the students were to follow the advice of Prof. Johnson he would fall far short of the desired goal. Ignoring the human phase, which so intimately concerns the work and life of the engineer, has caused many good men to "fall by the wayside."

On the whole, we think the editors would do well to revise this compilation of addresses and separate the "chaff from the wheat" before recommending that it be placed on the library shelf for reference. While most of the addresses are admirable they are rather too scattering in their nature to permit of their use in this form as a text book. WILLIS E. HALL.

Die Polarimetric der Erdöle. By M. A. RAKUSIN. 8vo. 404 pp. Verlag für Faehliterature. Berlin, 1911. Price, $4.00.

This book was apparently published for the purpose of bringing down to date the controversy on the method of formation of natural petroleum. It is divided into two sections, theoretical and experimental.

In the theoretical portion, 200 pages are devoted to a comprehensive review of the history of investigations on optical activity and racemized crude oils, and to discussions of these investigations from the standpoints of pure, analytical and physical chemistry, physics and geology.

The results of the investigation of about 100 European crudes, heretofore unpublished, are discussed from the various standpoints. Day's filtration experiments are also discussed rather fully and are further elaborated.

In the experimental portion some 30 pages are devoted to the methods of fractional distillation. This is followed by 150 pages, including numerous tables, of results of the fractional distillation of a large number of European crudes along with their polarimetric measurements. These results are very interesting, and are of great importance for the purposes of comparison.

No attempt is made to show that the polariscope is of any value in the petroleum laboratory, other than as suggesting a possible method for the detection of the geographical source of a sample. Nevertheless, a few figures are given in one section, seemingly to show that the optically more active fractions from some crudes were the more viscous.

The book is well worth the reading by any oil chemist, as it contains suggestions which are certain to be of value in the refinery.

The references to the contributions of other investigators in this field are numerous and will be valuable to any one looking up the subject. GAIL MERSEREAU.

NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Chemists' Club, New York

Alcohol, Wood—, Acetic Acids, Acetates, Acetone. By LOUIS CALVET. 8vo., 367 pp. $1.25. Ch. Béranger, Paris.

Alkaloid Chemistry, 1908-1911. By J. SCHMIDT. L. 8vo. $2.25. Ferdinand Enke, Stuttgart. (German.)

Analysis, Chemical—. By B. M. MARGOSCHES. L. 8vo. $0.60. Ferdinand Enke, Stuttgart. (German.)

Analytical Chemistry; Short Text-book of—; Vol. I. Qualitative Analysis By F. P. TREADWELL. 7th Ed. 8vo., 512 pp. $2.50. Vienna, 1911. (German.)

Assaying; Manual of Fire —. By C. H. FULTON. 2d Ed. 8vo., 236 pp. $2.00. McGraw-Hill Book Co., New York.

Chemical Works, Their Design, Erection and Equipment. By L. L. DYSON AND S. S. CLARKSON. 8vo. D. Van Nostrand Co., New York.

Chemistry, Yearbook of—: Vol. XX. 1910. By RICHARD MEYER. 8vo. $4.75. Friedrich Vieweg & Sohn, Brunswick. (German.)

Coals Available for the Manufacture of Illuminating Gas. By A. H. WHITE AND PERRY BARKER. 8vo., 75 pp. *Bureau of Mines, Bulletin* **6.**

Distillation, History of the Pharmaceutical-Chemical— Apparatus. By HERMAN SCHELENZ. Sm. 8vo., 169 pp. Presentation Ed. Schimmel & Co., Miltitz. (German.)

Electro-Analysis. By EDGAR F. SMITH. 5th Ed. 8vo., 332 pp. $3.00. Philadelphia, 1911.

Emery and the Emery Industry. By A. HAENIG. 8vo., 104 pp. D. Van Nostrand Co., New York.

Engineering Valuation of Public Utilities and Factories. By HORATIO A. FOSTER. D. Van Nostrand Co., New York.

Fertilizers, Report on Analyses of Samples of— Collected by the Commissioner of Agriculture during 1911. By E. L. BAKER. 8vo., 101 pp. *New York Agricultural Experiment Station, Bulletin* **341.**

Fertilizers, The Use and Production of Commercial—. By FRANK K. CAMERON. *U. S. Senate Document* **190,** Washington, D. C.

Flour, Effect of Common Mill Fumigants on the Baking Qualities of Wheat—. By G. A. DEAN AND C. O. SWANSON. 8vo., 207 pp. *Kansas State Agricultural College Experiment Station, Bulletin* **178.**

Granites of Connecticut. By T. N. DALE AND H. E. GREGORY. 8vo., 137 pp. *U. S. Geological Survey, Bulletin* **484,** Washington, 1911.

Illuminating Gas, Text-book of the— Industry. By W. BERTELSMANN. Vol. II. L. 8vo., 984 pp. $8.50. Stuttgart, 1911.

Inorganic, A Text-book of— Chemistry. By A. F. HOLLEMAN. 4th Ed. 8vo., 505 pp. $2.50. John Wiley & Sons, New York.

Light, The Chemical Action of—. By F. WEIGERT. L. 8vo., 114 pp. $1.00. Stuttgart, 1911.

Maple Sirup, A Study of—. By A. MCGILL. 8vo., 41 pp. Laboratory of the Inland Revenue Department, Ottawa, *Bulletin* **228.**

Metallurgy of Iron and Steel. By BRADLEY STOUGHTON. 2nd Ed. 8vo., 560 pp. $3.00. McGraw-Hill Book Co., New York.

Organic Chemistry, The Methods of—. By THE WEYL. Vol. II. 8vo., $14.00. Georg Thieme, Leipzig. (German.)

Organic, The Identification of— Compounds. By G. B. NEAVE. D. Van Nostrand Co., New York.

Organic, Short Text-book of— Chemistry. By A. BERNTHSEN AND A. DARAPSKY. 11th Ed. 8vo., 668 pp. $3.00. F. Vieweg & Sohn, Brunswick.

Paints, White Lead and Zinc White—. By G. PETIT. Cr. 8vo., 100 pp. $1.00. Scott, Greenwood & Son, London. (Translation.)

Paper: Its Manufacture and the Industry. By P. PUGET. 8vo., 450 pp. $1.00. Paris, 1911. (French.)

Peat, The Uses of— for Fuel and other Purposes. By CHARLES A. DAVIS. 8vo., 214 pp. *Bureau of Mines Bulletin* **16.**

Pharmacy, Encyclopedia of—. By J. MOELLER AND H. THOMS. Vol. XIII. 2d Ed. L. 8vo., $63.00. Vienna, 1904–1912. (German.)

Poisoning, Occupational—, its Occurrence, Characteristics, Treatment and Prevention. By J. RAMBOUSEK. L. 8vo., 431 pp. $3.00. Leipzig, 1911. (German.)

Potash Salts: Their Uses and Occurrence in the United States. By W. C. PHALEN. 8vo., 25 pp. U. S. Geological Survey, Advance Chapter, Mineral Resources 1910, Washington, 1911.

Saltpetre, The Indian— Industry. By J. W. LEATHER AND J. N. MUKERJI. L. 8vo., 19 pp. $0.25. Agricultural Research Institute, Pusa, India, *Bulletin* **24.**

Sewage, The— of Sea Coast Towns. By HENRY C. ADAMS 8vo., 142 pp. $2.00. D. Van Nostrand Co., New York.

Soil, Determination of Colloids in—. By C. HASSLER. 8vo., 65 pp. $0.50. Munich, 1911. (German.)

Sugar, Chemical-Technical Vademecum for— Manufacturers. By A. GROEGER. Vol. III. L. 8vo., 1645 pp. $11.00. Leipzig, 1911. (German.)

Sugar, A Handbook of— Analysis. By C. A. BROWNE. 8vo., 800 pp. John Wiley & Sons, New York.

Terpentine, Wood—: Its Production, Refining, Properties and Uses. By F. P. VEITCH AND M. G. DONK. 8vo., 76 pp. *U. S. Dept. of Agriculture, Bureau of Chemistry, Bulletin* **144.**

Varnishes, The Manufacture of— and Kindred Industries. By J. G. MCINTOSH. Vol. III. 2d Ed. 8vo. D. Van Nostrand Co., New York.

RECENT JOURNAL ARTICLES OF INTEREST TO THE INDUSTRIAL CHEMIST.

Ammonia, Plants for Making Sulfate of—. By C. G. ATWATER. *Progressive Age,* Vol. XXX, 1912, No. 1, pp. 15–21.

Ammonia, Sulfate of— Manufacture. By HOWELL FISHER. *Progressive Age,* Vol. XXX, 1912, No. 1, pp. 23–25.

Explosions, The Causes and Prevention of Coal Mine—. By EDWARD K. JUDD. *School of Mines Quarterly,* Vol. XXXIII, 1911, No. 1, pp. 65–71.

Explosives, Some Modern Developments in Methods of Testing—. By CHARLES E. MUNROE. *Annual Report Smithsonian Institution,* 1910, pp. 291–306.

Furnace, Calculations of— Charges. By REGIS CHAUVENET. *Metallurgical and Chemical Engineering,* Vol. X, 1912, No. 1, pp. 36–39.

Gold, Volatilization of— and Silver from their Copper Alloys. By EDWARD F. KERN AND ALBERT A. HELMROD. *School of Mines Quarterly,* Vol. XXXIII, 1911, No. 1, pp. 34–64.

Oils, New Philippine Essential—. By BENJAMIN T. BROOKS. *Philippine Journal of Science,* Vol. VIA, 1911, No. 4, pp. 333–351.

Paper Mill Economy. By JOHN W. BRASSINGTON. *Paper,* Vol. VI, 1912, No. 3, pp. 13–15.

Potash, Progress of Search for— in the United States. By H. S. GALE. *American Fertilizer,* Vol. XXXV, 1911, No. 13, pp. 21–37.

Sewage, The Relation of the Putrescibility of the Settling and Non-Settling Suspended Matter in—. By ARTHUR LEDERER. *Engineering Record,* Vol. LXIV, 1911, No. 26, pp. 733–734.

RECENT INVENTIONS

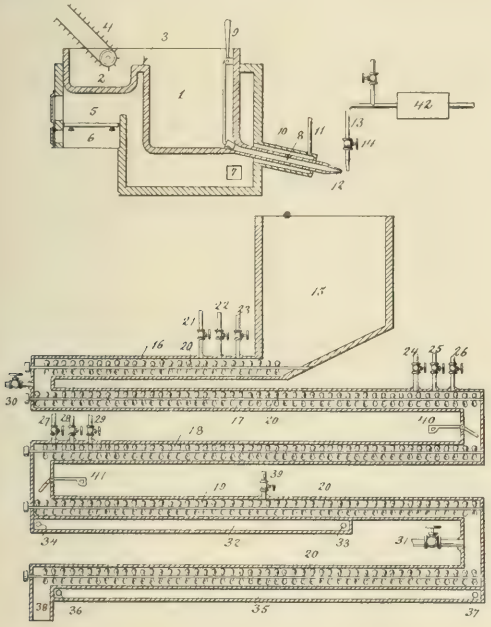
Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

CONTINUOUS PROCESS OF MAKING WHITE LEAD AND APPARATUS THEREFOR.

U. S. Patent No. 1,002,246, to Carleton Ellis, Montclair, N. J.

This invention is a process of making white lead in a continuous or non-cumulative manner, which makes the operation an automatic one from the time the lead is introduced into the melting pot up to the time when the finished white lead is ready to be packed for shipment.

The invention involves melting the lead, preferably in a tank equipped with a melting pot and molten lead reservoir, in comminuting the molten lead by means of a jet of compressed



air, inert gas, steam or water, collecting the comminuted product and maintaining it by such means as an extensive conveying system, in contact with air and carbon dioxid and water or steam or both, until the lead has become converted into basic carbonate of lead or hydrated carbonate of lead, corresponding to the accepted formula for white lead, and finally freeing the product from its moisture.

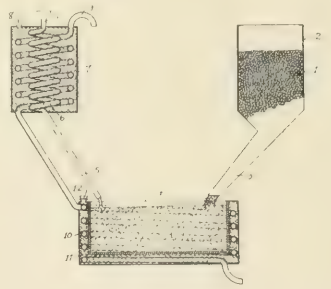
The illustration shows apparatus in which the process is carried out.

PROCESS OF MAKING SUPERPHOSPHATES.

U. S. Patent No. 1,003,681, to Rinaldo Williams, of Birmingham, Alabama.

This invention is a process for the manufacture of superphosphate or acid phosphate particularly where phosphate rock containing a relatively large percentage of impurities, such as oxid of iron, alumina, etc., is treated with sulfuric acid to form available phosphoric acid in the form of $CaO_2H_3OP_2O_5$ or $2CaOH_2OP_2O_5$.

The patentee has found that sulfuric acid will not act on the impurities in the phosphate rock, or at the most will act but little where the reaction between the acid and phosphate takes place at a low temperature. In other words, when the sulfuric acid and crushed phosphate rock are mixed in the pan or retort if the mixture and, if necessary, the pan itself be kept cool or below 100° F., the sulfuric acid will act only on the tricalcic phosphate in the rock, converting the latter almost entirely into available phosphoric acid in an acid phosphate



mixture which will contain in addition to said acid phosphate only the quantity of impurities originally in the phosphate rock, the same constituting practically a fixed element.

TREATMENT OF PETROLEUM.

U. S. Patent No. 1,002,570, to J. A. Dubbs, Santa Monica, Cal.

This invention relates to the distillation of petroleum to produce asphalt and asphaltic residual bodies.

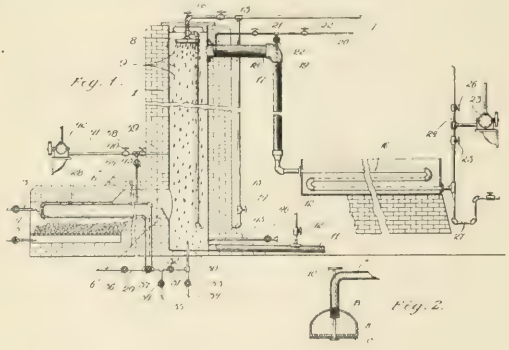


Fig. 2.

The process consists in treating petroleum to dry, and free the same from water, distil or produce asphalt therefrom, consisting in continuously causing the petroleum to drop, *in vacuo*, in the presence of ascending currents of combustion gases to drive off the lighter products from each of said drops while in suspension and collecting the asphaltic residuum below the heat zone, the size of the drops being varied according to the ascending heat and to the product desired.

The illustration shows apparatus in which the process is carried out.

MARKET REPORT.

(AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF JANUARY.)

Full List of Weekly Quotations, see "Oil, Paint & Drug Reporter."

ORGANIC CHEMICALS.

Acetanilid	Lb.	20½	@	23
Acetone (drums)	Lb.	13⅞	@	15¾
Alcohol, grain (188 proof)	Gal.	2.56	@	2.58
Alcohol, wood (95 per cent.)	Gal.	50	@	52
Alcohol, denatured (180 proof)	Gal.	40	@	42
Amyl Acetate	Gal.	3.00	@	3.25
Acetic Acid	C.	1.79⅜	@	1.99⅜
Aniline Oil	Lb.	10¾	@	11½
Benzoic Acid	Oz.	11¼	@	12
Carbon Tetrachloride (drums)	Lb.	7¾	@	8¼
Carbon Bisulphide	Lb.	7	@	12
Chloroform	Lb.	23	@	28
Carbolic Acid (drums)	Lb.	18	@	19¾
Citric Acid (domestic)	Lb.	38½	@	39
Camphor (refined in bulk)	Lb.	—	@	44
Dextrine (imported potato)	Lb.	6	@	7
Dextrine (corn)	C.	2.11	@	2.25
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	16½	@	17
Iodoform	Lb.	2.95	@	3.00
Oxalic Acid	C.	7¼	@	7½
Pyrogallic Acid (bulk)	Lb.	1.35	@	1.45
Salicylic Acid	Lb.	32	@	34
Starch (corn)	C.	1.80¾	@	1.94¾
Starch (potato)	Lb.	5¼	@	5½
Starch (rice)	Lb.	7	@	8
Starch (wheat)	Lb.	4⅞	@	5¼
Tannic Acid (regular in bulk)	Lb.	68	@	70
Tartaric Acid, crystals	Lb.	30¼	@	30¾

INORGANIC CHEMICALS.

Acetate of Lime (gray)	C.	2.18¾	@	2.23¾
Acetate of Lead (brown, broken)	Lb.	7¾	@	8
Alum (lump)	C.	1.75	@	2.00
Ammonium Carbonate, domestic	Lb.	8	@	8¾
Ammonium Chloride, gray	Lb.	6⅛	@	6¾
Aluminum Sulphate	C.	90	@	1.75
Ammonium Vanadiate	Oz.	41	@	50
Aqua Ammonia (drums) 16°	Lb.	2¼	@	2½
Arsenic, white	Lb.	2⅜	@	2¾
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Barium Chlorate	Lb.	15	@	17
Barium Chloride	C.	1.90	@	2.25
Barium Nitrate	Lb.	5½	@	6¼
Borax, crystals (bags)	Lb.	3½	@	4
Boric Acid, crystals	Lb.	7	@	7½
Bromine, bulk	Lb.	25	@	30
Bleaching Powder (35 per cent.)	C.	1.21	@	1.30
Barytes (prime white, foreign)	Ton	18.50	@	22.50
Blue Vitriol	Lb.	4¾	@	5¼
Calcium Chloride	C.	65	@	90
Calomel, American	Lb.	90	@	92
Chalk (light precipitated)	Lb.	4½	@	6
Cobalt Oxide	Lb.	80	@	1.00
China Clay (imported)	Ton	11.50	@	18.00
Feldspar	Ton	8.00	@	12.00
Fuller's Earth, powdered	C.	80	@	85
Green Vitriol (bags)	C.	60	@	85
Hydrochloric Acid (18°)	C.	1.15	@	1.55
Hydrochloric Acid (22°)	C.	1.45	@	1.75
Iodine (resublimed)	Lb.	2.60	@	2.65
Lead Nitrate	Lb.	8⅛	@	8⅝
Lithium Carbonate	Lb.	67	@	70
Magnesite (raw)	Ton	10.00	@	11.00
Mercuric Chloride	Lb.	81	@	84
Nitric Acid, 36°	Lb.	3⅞	@	4¼
Nitric Acid, 42°	Lb.	4⅞	@	5¼
Phosphorus	Lb.	45	@	1.00
Phosphoric Acid, s. g. 1.75	Lb.	22	@	26
Plaster of Paris	C.	1.50	@	1.70
Potassium Bromide	Lb.	31	@	34
Potassium Permanganate (bulk)	Lb.	9⅜	@	10¾
Potassium Cyanide (bulk)	Lb.	20	@	24
Potassium Iodide (bulk)	Lb.	2.10	@	2.15
Potassium Chlorate, crystals	Lb.	8¼	@	9½
Potassium Nitrate (crude)	Lb	4½	@	5
Potassium Bichromate, 50°	Lb.	7⅜	@	7¾
Pumice Stone	Lb.	2	@	4
Quicksilver	Lb.	60¼	@	61¼
Salt Cake (glass-makers)	C.	55	@	65
Silver Nitrate	Oz.	34½	@	36¾
Soapstone in bags	Ton	10.00	@	12.00
Sodium Acetate	Lb.	4¼	@	5
Sodium Chlorate	Lb.	8¼	@	9½
Sodium Bicarbonate (English)	Lb.	2¾	@	3
Sodium Bichromate	Lb.	5⅝	@	6
Sodium Bisulfite (not incl. pkg.)	C.	75	@	1.37½
Sodium Hydroxide, 60 per cent	C.	1.75	@	1.80
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent., spot	C.	—	@	2.12½
Sodium Silicate (liquid)	C.	65	@	1.50
Sodium Stannate	Lb.	9¾	@	10
Strontium Nitrate	Lb.	7¼	@	8
Sulphur, Roll	C.	1.85	@	2.15
Sulphur, Flowers	C.	2.20	@	2.60
Sulphuric Acid, 60° B.	C.	85	@	1.00
Talc (American)	Ton	15.00	@	20.00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	—	@	13
Tin Oxide	Lb.	49	@	51
Tin Chloride (36°)	Lb.	11	@	11½
Zinc Chloride (granulated)	Lb.	4¼	@	4½
Zinc Sulphate	Lb.	2¼	@	2½

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	40	@	45
Black Mineral Oil, 29 Gravity	Gal.	12	@	12½
Castor Oil (No. 3)	Lb.	9½	@	10½
Ceresin (yellow)	Lb.	8¼	@	15½
Corn Oil	C.	5.95	@	6.00
Cottonseed Oil (crude), f. o. b. mill	Gal.	31½	@	32
Cylinder Oil (light, filtered)	Gal.	19½	@	20
Japan Wax	Lb.	9	@	9¼
Lard Oil (prime winter)	Gal.	75	@	83
Linseed Oil (double-boiled)	Gal.	—	@	76¼
Paraffine Oil (high viscosity)	Gal.	23½	@	24
Paraffine (crude 120 @ 122 m. p.)	Lb.	3	@	3⅛
Rosin Oil (first run)	Gal.	36	@	—
Spindle Oil, No. 1	Gal.	14	@	14½
Sperm Oil (bleached winter) 38°	Gal.	76	@	78
Stearic Acid (double-pressed)	Lb.	10¼	@	10½
Tallow (acidless)	Gal.	63	@	65
Tar Oil (distilled)	Gal.	30	@	31

METALS.

Aluminum [No. 1 ingots]	Lb.	18½	@	19
Antimony (Hallet's)	Lb.	7⅜	@	7⅝
Bismuth (London)	Lb.	—	@	1.80
Copper (electrolytic)	Lb.	13.81	@	14.08
Copper (lake)	Lb.	14.02	@	14.29
Lead, N. Y.	Lb.	—	@	4.45c
Nickel	Lb.	40	@	48
Platinum (refined)	Oz.	—	@	46.00
Silver	Oz.	54½	@	55
Tin	Lb.	—	@	44½
Zinc	Lb.	6.22	@	6.39

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume IV MARCH, 1912 No. 3

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Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered at the Post-Office, Easton, Pa., as Second-class Matter.

TABLE OF CONTENTS.

EDITORIALS:

Conservation ... 160

MINERAL WASTES SYMPOSIUM:

Carbon Wastes. By J. A. Holmes ... 160
Zinc Losses. By W. H. Bassett ... 164
Need of Special Alloys for Special Purposes. By W. H. Bassett ... 167
Waste and Conservation of Potash and Phosphoric Acid. By F. K. Cameron ... 169
Losses of Combined Nitrogen. By John D. Pennock ... 172
The Abuse of Brand. By A. D. Little ... 178
The Relation of the Silicate Industries to Conservation. By A. V. Bleininger ... 180
New Uses to Reduce Abuses in Conservation. By W. R. Whitney ... 182
Mineral Losses in Gases and Fumes. By F. G. Cottrell ... 182
Miscellaneous Mineral Wastes. By Chas. L. Parsons ... 185

ORIGINAL PAPERS:

A New Method for Testing Paint Films and Preservative Coatings for Iron and Steel. By W. C. Slade ... 189
A Short Method for the Determination of Soluble Arsenic in Commercial Lead Arsenates. By B. E. Curry and T. O. Smith ... 198
Valuation of Fluorspar. By E. Bidtel ... 201
Determination of Manganese in Steel. By James J. Boyle ... 202
Carbon Dioxide: Its Volumetric Determination. By Leon T. Bowser ... 203
The Value of the Higher Phenols in Wood-Preserving Oils. By Samuel Cabot ... 206
Composition of Dry Gluten and its Relation to the Protein Content of Flour. By Geo. A. Olson ... 206
A Comparative Study of Methods for the Determination of Hard and Total Soft Resins in the Hop. By H. V. Tartar and C. E. Bradley ... 209
The Chemistry of Anaesthetics, IV: Chloroform. By Charles Baskerville and W. A. Hamor ... 212

LABORATORY AND PLANT:

A Modified Wiley Extraction Apparatus. By W. D. Richardson and E. F. Scherubel ... 220
A Substitute for the Blast Lamp. By W. A. Ernst ... 221
A Convenient Filtering Apparatus. By C. S. Williams, Jr. ... 222
An Improvement on the Kjeldahl Distilling Apparatus. By W. L. Hadlock ... 222

COMMITTEE REPORTS:

Committee on Fertilizer Legislation. Fertilizer Division ... 223
Committee on Potash. Fertilizer Division ... 224
Committee on Phosphate Rock. Fertilizer Division ... 225
Committee on Nitrogen. Fertilizer Division ... 225
Committee on Standard Specifications and Methods of Analysis. Industrial Division ... 225
Committee on Definition of Industrial Terms. Industrial Division ... 226
Committee on Professional Code of Ethics. Industrial Division ... 226

NOTES AND CORRESPONDENCE:

A Note on Sampling. By W. J. Sharwood ... 227
Laboratory Preparation of Litmus Paper ... 229
Perilla Oil ... 229
Barleys Exhibited at the Second International Barley and Hop Prize Exhibit ... 230
Eighth International Congress Notes ... 230

OBITUARIES:

Dr. Naokichi Matsui ... 230

CONSULAR AND TRADE NOTES:

German Bronze-Powder Industry ... 231
Electrolytic Recovery of Zinc ... 231
Sulphur Mines in Mexico ... 232
Amalgamation of British Cement Companies ... 232
Argentina's Wine Industry ... 232
Petroleum Output of the World ... 232
Oil from Sunflower Seed ... 232
Gas Production and Consumption in England ... 232

BOOK REVIEWS:

Some Chemical Problems of To-day; The Manufacture of Chemical Manures; The Technical Analysis of Brass and the Non-ferrous Alloys; Pure Foods. Their Adulteration, Nutritive Value and Cost; Plant Food. Its Sources, Conservation, Preparation and Application ... 233

NEW PUBLICATIONS ... 233

RECENT INVENTIONS ... 236

MARKET REPORT ... 238

EDITORIALS

CONSERVATION.

In publishing the symposium upon conservation which occupies a large portion of this number of the Journal, a great service is being done. It should be realized that the problem of conservation is largely a chemical one and that the leaders in industrial chemistry have serious responsibility in respect to it.

In reference to many of the materials extracted from the earth there are certain common factors. Most of them have been exploited for thousands of years. However, the drafts upon the reserves of the earth as compared with its total capacity were small until the beginning of the nineteenth century. From the dawn of civilization until that time the amounts of fuels and metals mined had been so inconsiderable that there was no need of thought for the morrow. By the philosophers of any time before the nineteenth century, it might have been asserted that the stores of these substances were so large as compared with the need for them that they would last through the indefinite future.

In the early half of the nineteenth century there appeared a phenomenal increase in the drafts upon the various mineral resources; but still the amounts demanded were not so large as to suggest forethought. Then came the latter half of the century, the age of scientific advance and invention, the industrial and commercial age. Any forecasts as to the future life of the mineral resources which might have been made upon earlier data became worthless; and the closing decade of the nineteenth century and the first decade of the twentieth century show the rate of exploitation ever accelerated. Indeed in the United States for many substances the output has doubled in ten years or less, including the all-important coal and iron. So far as this is true, it means that the output of the first decade of this century has been more than equal to that of all previous decades.

In this modern era of stable government for great nations, with peace general, war exceptional, instead of war general and peace exceptional; with the development of agriculture, manufacture, and transportation, there has come an enormous increase in population. This increase will continue until the habitable areas of the world are fully occupied. The natural resources must be so handled as to meet the needs of these billions of people through hundreds of thousands, probably millions, of years to come. From the point of view of coming generations, the problem of conservation is the most fundamental and far-reaching of those that are presented to the race.

The conservation movement, following the White House conference in 1908, was taken up with great enthusiasm all over the country, and became almost at once a national policy; but the successful solution of the problem of conservation is one which will require the work of the leaders in applied science through many years to come. Already the popular interest in the movement is waning. Now is the time when the staying powers of those who appreciate its importance is required. It is fortunate for the nation that the industrial and engineering chemists fully appreciate this situation, and are striving not only to keep the conservation movement alive but to push it forward with increasing power.

CHARLES R. VAN HISE.

MINERAL WASTES SYMPOSIUM

CARBON WASTES.

By J. A. HOLMES.

In opening the discussion on the question of waste, it may be proper to say just a word or two on the general question of waste and the possibilities of its reduction.

The Bureau of Mines, created about one and a half years ago, has had set before it two general purposes which illustrate the way that the Federal Government, as a government, is interested in this matter of preventing waste. One of these purposes is to lessen the loss of life, and the other is to lessen the waste of resources in the mining, metallurgical and general mineral industries of the country. Both of these lines of endeavor are essential to the permanent welfare of the nation as a whole.

In discussing problems of this kind under the topics of waste and conservation, we must bear in mind the fact that conservation, which in name though not in reality is a comparatively modern invention, has been used and abused to such an extent that while it has become more or less popular in the country-at-large, it has also become decidedly unpopular with certain classes of people in this country. I think it is the province of the chemists and mining engineers, more than any other classes of people in the country, to give conservation the basis in practical affairs which it ought to have.

I know that many of us, from the geologic and engineering side, have been trying for years to get along without chemists or with fewer chemists. But we have found this impossible; instead, we have been almost swamped with the constantly increasing need for more chemists. It is therefore eminently proper, it seems to me, to discuss these waste problems with and among chemists.

The topic in this symposium which has been assigned to me, namely "Carbon Wastes," illustrates one or two general principles which also I trust I may be pardoned in calling attention to in opening this dis-

cussion, and that is, what is a real waste may or may not now be a preventable waste in the present state of knowledge or under existing economic conditions. Thus the waste in the utilization of coal; those who are less familiar with the mining industry than you are with the metallurgy, may not be aware of the fact that for every ton of coal brought to the surface in the bituminous or soft coal mines of this country, not less than one-half a ton is left under the ground, and it will not be possible to bring it to the surface in the future at any reasonable cost, if at all. But more shocking still is the fact that in our anthracite coal fields, which are so limited in extent as to be confined to a territory comprising less than four hundred square miles, even with all modern improvements, not more than 50 per cent. of the anthracite coal of the areas mined is being brought to the surface. The remainder of it, now aggregating 80,000,000 tons a year, is being left underground in such condition as to make its future recovery difficult if not impossible.

In the early days of anthracite mining there was brought to the surface an average of between 30 and 40 per cent. of the coal, so that from 60–70 per cent. remained under the ground, which was sufficient to give strength to the proof; and to-day mining engineers are bringing to the surface a part of the coal which was left in the mines 30 or 40 years ago. But as the percentage of coal mined has increased from time to time, the possibility of recovering what is left behind diminishes. It has been estimated that since the beginning of coal mining in the United States, more than 2,000,000,000 tons of anthracite coal and 3,000,000,000 tons of bituminous coal have been left underground in such condition as to make its future recovery doubtful or impossible.

I know of no other American industry which to-day is in so deplorable an economic condition as is the bituminous coal industry. The operators, unable under existing laws to combine and fix prices of coal or any trade agreements, are adopting what appears to be the only alternative—ruinous competition, which encourages or enforces wasteful and dangerous mining. It seems essential that Federal or joint state legislation be enacted authorizing such reorganization of this great industry as will permit reasonable returns on the money invested and at the same time properly safeguard the public interests. You realize that it is often less expensive per ton for the operator to bring the first half of his coal to the surface than it is for him to bring out the remaining half, because this second half will support the roof while the first half is being removed; but while he removes the second half he must often temporarily support the roof with timbers; this entails additional expense to meet which there is generally neither an accumulated surplus from which to draw, nor a temporary profit from which to meet this extra expense; hence the coal is abandoned. It is only fair to the coal operator that he is not in the mining business for his health, but to make a living by earning a reasonable return on his investment. Therefore, what we may consider a waste may be a necessary waste under existing economic conditions; a waste, however, that is preventable and should be prevented by improvements in our economic conditions, and necessary legislative requirements.

Therefore, I think it is up to the people of the United States before condemning the coal operator for this waste, to make it profitable and possible for him to mine all the coal and then to see that he does it. I shall not now attempt, with the limited time set apart for this discussion, to inflict you with statistical details. The figures I have given you represent some of the largest preventable losses in carbon. Other large wastes of carbon come in the burning of coal for power and lighting purposes, flue losses, radiation losses, losses in imperfect burning, losses in the engines, and the transformation of steam into mechanical work, or electric light. Many of these losses we cannot see how to avoid now. They may be, for years to come, necessary losses. Both chemists and engineers should do everything in their power, and they are doing much, to reduce these losses and render them preventable. You and I to-day perhaps pay all that we ought to pay for coal laid down at our furnaces, but not enough of that goes back to the mine to repay the operator and the miners for the cost of their labor and other mining expenses. The coal repays to the operator and the laborer together scarcely more than $1.00 per ton for the responsible and dangerous work of getting out and putting on board the cars most of the bituminous coal in the United States. The operator in Europe gets twice as much per ton out of his coal after getting it on board cars, as does the American operator. I know cases where the profit per ton on European coal at the mine is greater than the total price received for American coal of the same quality on board cars at the mines. Our American operator is right when he says that he cannot prevent this waste, nor can he spend much on safety devices, at the present prices of coal. With facts and justice on his side, he says: "What can we do? We have to earn a living."

Our waste of natural gas is a crime, and thoroughly discreditable to the nation. It is far worse than the waste of coal. The statistics for last year (1910), according to the Geological Survey, showed that some 480,000,000,000 cubic feet of gas were turned into the atmosphere and forever lost. In the above as in other cases, the individual operator finds it easier to save a part, than all, of these resources, yes, cheaper for him to waste a large part of these resources than to save all. In the case of natural gas he says: "I want to get oil, and if I can get the oil cheaper by letting the gas escape, that is the operation I will pursue." And the state and the nation stand by and watch the operation.

In connection with petroleum, we have less losses than in almost any other branch of the American fuel industry. The losses in this branch of the industry, which may be considered in any sense preventable losses, probably do not exceed 10 per cent.; but a loss of 10 per cent. in a great industry like the petroleum industry is a serious matter and worthy of con-

sideration. The waste, if such it be called, in the petroleum industry, is rather that of the misuse of certain products, but that may be passed by for the present.

When the waste products prove injurious in the atmosphere a new factor is brought into place, which aids in developing prohibitory legislation; but prohibitory legislation without the aid of the chemist accomplishes little. If we turn some 4,000 tons of sulphur per day into the atmosphere, as SO_2, the chemist must discover how that sulphur can be caught and utilized again, or stored until the need for it has developed. If we are now turning more than 100 tons of arsenic into the atmosphere daily, the chemist must show us how we can use this arsenic. The operator says: "You must show me some way in which I can prevent these losses and still make my business pay."

A remedy of one waste may bring about a waste in some other direction. In coal mining, for example, we have been trying to stop the gas explosions, and found that one way to stop them is to pump two or three hundred thousand cubic feet of air through the mine and sweep out these gases; but we found that in doing this the coal dust itself becomes, during the cold weather, more dangerous than the gas, because this very ventilation keeps it dry. Then when we turn exhaust steam through the mine, trying to moisten the coal dust and cause it to settle, and trying to prevent that being explosive, we find we have developed conditions in that mine which in turn are especially favorable to the hookworm and other trouble.

So we can develop along the best lines only by coöperation between the chemists and the engineers, in trying to find out what wastes can be prevented to-day, and how the necessary waste of to-day can be made a preventable waste of to-morrow on a fair, business-like basis.

There are many other examples of extensive and serious carbon waste in this country. Thus, in the coking industry the beehive coke ovens have turned into the atmosphere more than 100,000,000,000 cubic feet of valuable gas which, if properly treated, will yield not only gas but other important carbon by-products.

There is also turned loose into the atmosphere from the blast furnaces of the country enormous quantities of valuable gas. During the past few years there has been considerable progress made in the utilization of this gas for power purposes, but a large portion of it still goes to waste.

So, too, there is a loss of large quantities of carbon growing out of the making of coke by the beehive instead of the by-product process. There are still other important carbon wastes, if time permitted even their mention.

In this discussion I have made no attempt to cover the losses of carbon in the consumption or the waste of forest products, lumber, etc., but in any complete treatment of the subject this, of course, would deserve consideration.

The important proposition before us is, knowing something of the extent of this waste, to find the remedy.

DISCUSSION.

MR. KENT:

I enter this discussion by request of Dr. Holmes. I have been familiar with the work done by him for a great many years, and just want to supplement what he says on the question of wastes of coal in mining operations, by saying something with regard to the wastes of coal after it is mined and is in the market. As he says, 50 per cent. of the coal now mined is wasted in the mines, and then of the 50 per cent. that gets into the market, perhaps 50 per cent. of that coal is wasted by the consumer. I have no statistics on this, but it is a pretty good guess.

In the best boiler practice, we can get nearly 80 per cent. efficiency out of the coal, but such a high efficiency is reached only when we have the aid of the chemist to control the composition of the waste gases. The latest boiler experiments indicate that the condition of maximum efficiency is that the free oxygen in the gases ranges within the narrow limits of 5 and 8 per cent. But we have as yet no gauge or indicator by which the fireman can tell whether the gas is of the proper composition and whether he is firing right or not. He has a steam gauge to tell him the pressure of the steam, but whether he is firing that fire so as to have between 5 and 8 per cent. oxygen, he does not know. So instead of 70–80 per cent. efficiency in boilers, we have in practice only 40–60 per cent.

Now as to steam, we all know that there is a tremendous loss in the steam engine, and in the gas engine too; but there is one feature of loss that is not generally considered; that is, the increase in the use of power which is not really necessary except to satisfy our desire for luxury: for instance, it takes four times as much coal to take a vessel across the Atlantic in four days as it would in eight days. Of course, burning four times the amount of coal, enabling it to cross the Atlantic in four days, may be offset by a saving in the time of passengers and crew, but as far as the coal is concerned, high speed involves a tremendous waste.

There is also a waste here in Washington and in every other city, an immense waste of coal—in the electric lights used purely for advertising purposes.

We are burning up coal at an ever increasing rate and charging the atmosphere with carbon dioxide, which floats around the world until it is absorbed by vegetation. It is hoped that the agricultural chemists some day will be able to devise a process by which they can catch some of that carbon dioxide and put it back into the soil and produce carbon compounds, such as alcohol, which we can use for heat and light and power, and thus diminish the waste of coal.

MR. WHITNEY:

I rise to oppose the suggestion of Mr. Kent that you are wasting too much energy in lighting the great white ways. Owing to recent reductions in costs of producing light, you are nowhere near using your "velvet" in lighting your great white ways to which he referred.

MR. LITTLE:

The paper industry is one which is peculiarly conservative. They are not particularly anxious to be shown. I remember an early experience of mine when, after much trouble, I finally made a contract with a large paper mill. The first thing I did when I went there was to collect samples of all of their waste waters, and determine the amount, proportion and kind of material that was going into the stream. The mill had never paid, though it was well located. One reason for their failure to pay a dividend, as I found, was that 17 per cent. of the product was going down the river. I told the manager about it. Well,

he paid my salary for a year and never allowed me to come into the mill again.

Steps have already been taken to utilize a large quantity of the timber waste for the production of ethyl alcohol. Some of our lay friends have expressed skepticism as to the possibility of getting rain alcohol from wood, but everything becomes clear when we simply tell them that we make it from the grain of the wood.

However, that industry is one which is bound to expand very largely. There is one plant in operation making two thousand gallons per day, and when the new plant comes in it will make from five to seven thousand gallons per day, and probably will be followed by many others of similar proportions.

The paper trade is not the only one that permits itself to indulge in needless waste and even the best intentions sometimes lead to extravagance. There is a story of an automobile concern which was led, by a laudable desire to maintain a dustless testing track, into sprinkling the track with twenty-seven barrels of cylinder oil.

MR. LOEB:

I should like to call attention to a plan which Professor Bone, of England, related to us recently in New York, and which seems to be well adapted toward reducing at least some of the waste of coal. It appears that considerable waste occurs through running dynamos of high capacity continuously at a low duty, merely to be ready for a maximum load at any time. They overcome this in England, especially in Yorkshire and Durham County, by coupling all the electric plants throughout the country in a single wiring system, so that each manufacturer can draw on all the combined dynamos of the region when he needs an excess of power, and transfer his own surplus when his demand is less than his actual capacity; in other words the entire group of plants insure each other against individual overloading and, consequently, need not keep excessively large units in operation. The saving resulting from this system in England is very large, according to Professor Bone.

MR. HERTY:

In connection with the enormous waste of wood in the southern lumber mills, I think it only fair to the southern lumberman to say this: They are fully aware now of the waste that is going on, and I do not suppose you will find any body of men in this country who are more anxious to avert that waste than the very men who are making it. What they are suffering from, however, is the lack of guidance in how to do it, or rational methods of how to avoid it. I have talked with a number of these men in years past, and they are alive, wide-awake, and anxious to know how to do it. That part of it, the educational problem, is finished, so far as arousing interest is concerned.

What is to be avoided in the future is the men who are not scientifically trained, who are promoters of the worst type, who are crippling the work of the real scientific men of the country. I cannot point out to chemists any more resourceful field for work than this. I can assure you that these lumbermen are anxious to know how to help themselves in preventing this form of waste of the carbon of the country.

MR. COMEY:

Speaking of the paper industry: I was in the Adirondacks this summer and saw them cutting up spruce trees 100 feet tall and 2 feet or more in diameter into cordwood to send down to New York to make New York Journals. I think that is about as complete a waste of good material as can be found anywhere. Several thousand cords of that wood were used to make one Sunday edition of the *New York Journal*.

MR. PARR:

I simply want to mention one source of carbon waste which, at first thought, may be a little absurd, but any manufacturer appreciates the very considerable expense attached to the matter of crating, and when he begins to figure out especially that crating material is rather expensive to recover and put together again, he prefers to make a bonfire of that material rather than store it and utilize it again. A change is gradually coming into vogue in certain forms of cheap material, which will not make it so expensive as with the better grades of material that have been used in crating, but still there is a waste, and it is growing.

MR. BRENEMAN:

It may surprise many to know that in New York Bay, for a mile or two below the Narrows, I have seen, for many years past, accumulations of driftwood along the shore, sometimes as much as fifty cords of perfectly good wood, which could have been utilized to great advantage as kindling wood in the city if any one would take the trouble to collect and use it. The people along the shore get all the firewood they want from this driftwood, which is composed of lost or discarded timber from vessels, broken piles and lop from the city piers, carpenters' waste, etc. At Seagate, the western end of Coney Island, it used to be burned in large heaps to be rid of it.

MR. CALDWELL:

In connection with what has been said in regard to the waste of lumbermill materials, I may simply state that I visited not long ago a mill which made use of sawmill slabs, also sawdust, in the manufacture of producer gas. While I have no figures to report, I expect it was a very profitable operation, so that people are now becoming more wide awake to the necessity of using these waste materials. I do not think I can illustrate that any better than to relate the fond hope which somebody had the other day. He came into my laboratory with a cubic foot of dried swamp land, which of course contained an immense amount of carbon, and he expressed the hope that it might be used for fuel.

MR. BIRD:

In connection with the subject of carbon waste, a most crying need of conserving carbon is to correct what is going on now so extensively in the neighboring Appalachian mountains; namely, the burning of the forests, depredations by insects, etc. For a future supply of forest products, we must protect the young trees, and bring about a rational system of cutting the older trees.

MR. FRANKFORTER:

I have been interested in the matter of the lumber and wood waste in the lumber mills for a number of years. Actual experiments show that nearly 60 per cent. of the total weight of timber is wasted. Forty per cent. of the tree is the best that the lumber mill can do at the present time. I have seen trees, 8–12 feet in diameter, cut 20 feet above ground in order to avoid the resin which is frequently so abundant as to make the lower part of the tree of little value for lumber. You can imagine what the waste would be in trees of that type. On the Pacific Coast the mills save between 25 and 30 per cent. on the big trees.

MR. ROBERTS:

A rather unusual variety of utilization of a carbon waste product is involved in the proposal to extinguish fires and kill vermin in mines, ships and other enclosed places, by blowing the burnt gases from the furnaces into the burning compartment. The gases first are cleaned and cooled by a shower of water. The basic idea is the subject of an expired patent, but the earlier machinery was crude. An efficient machine for the purpose is covered by a recent patent (Harker, 1909, U. S. No. 915,431). The machine has been thoroughly tried out and approved by the Australian authorities, and the U. S. Public Health and Marine-Hospital Service is now installing one for trial on a quarantine steamer.

MR. HOLMES:

The practice in Belgium and Germany to-day of filling in the mines with sand and other materials known as flushing makes possible not only the taking out of all the coal, but prevents the settling of the surface, and it also prevents explosions and mine fires of which latter, in this country, we have so many. So there are many reasons why that ought to be done, and in European countries the added cost has not exceeded twenty-five cents per ton on the extra coal recovered by this flushing process.

The losses of carbon in many of these ways which have been mentioned, blast furnaces, cupolas, etc., are tremendous.

MR. PARSONS:

There is one point in connection with this question of carbon waste that has not been dwelt upon, and that is, the tremendous waste in carbon and in energy in the beehive coke oven. It has been figured, I believe, by Mr. Parker, of the Geological Survey, that the energy allowed to go to waste in the production of coke in this country alone amounts to one million horsepower per day, which is four times the amount of energy they hope to utilize in Sweden for the fixing of atmospheric nitrogen. They expect in two or three years to have 250,000 horsepower actually at work in fixing the nitrogen of the atmosphere, and there is actually one million horsepower going to waste in the coke industry in this country alone.

I doubt if this audience realizes that by the utilization of the new cup system of gathering turpentine in the South, probably thirteen million dollars has been saved in the turpentine industry.

ZINC LOSSES.

By W. H. BASSETT.

A considerable loss in the brass manufacturing industry arises through the volatilization of the zinc in the process of melting and alloying. This loss owing to want of reliable statistics cannot be even approximately estimated.

The copper losses in most of the more progressive manufacturing establishments are very small. These have not been difficult to take care of, but the zinc losses, on the other hand, have presented a much more difficult problem on account of the volatile nature of the metal.

Zinc melts at about 420° C. and boils at about 930° C. Copper melts at about 1080° C. and, in making brass, has to be sufficiently heated to take the zinc without chilling before it is all added. Brass for working is poured into iron chills, and must be sufficiently hot when cast to give a smooth surface free from cold sets and other flaws. On this account the pouring temperature for high brass is about 1050° C. The melting point of the alloy copper 70 zinc 30 is given by Charpy as 945° C., and that of the alloy 60 copper 40 zinc as 880° C. Two and one brass melts at approximately 920° C., that is, very nearly at the boiling point of zinc. It is consequently evident that, when most of the brasses are sufficiently fluid to pour freely, the zinc is rapidly distilling from them.

The actual loss of zinc, in flue dust and in zinc fumes which pass into the atmosphere in the melting and casting of brass for rolling, amounts to approximately 6 per cent. of the zinc used.

Most commercial brands of zinc carry both lead and cadmium. Either of these elements may run as high as 0.75 per cent. in the common brands used in brass-making. The cadmium in the Western brands average 0.30 per cent. to 0.50 per cent.

The composition of the flue dust from the fires in which brass is melted is interesting as it indicates a much more rapid volatilization of cadmium and lead than of zinc. Samples taken from flues in the casting shops of two different mills gave the following composition:

	"A." Per cent.	"B." Per cent.
Copper oxide	2.85	2.50
Iron oxide	2.43	...
Zinc oxide	32.13	24.74
Cadmium oxide	1.56	0.89
Lead oxide	0.31	1.92

Per cent. cadmium oxide amounts to 4.9–3.6 per cent., respectively, of the ZnO present.

In some instances we have found 6 per cent. as much cadmium oxide as zinc oxide. A search for cadmium in sheet brass made from zinc carrying $^1/_2$ per cent. of that element failed to reveal an amount sufficiently large for determination, indicating that in ordinary practice the cadmium is substantially all volatilized.

Part of the zinc lost by volatilization remains in the fluxes mixed with fine ashes as flue dust and part goes off into the atmosphere. Numerous suggestions have been made for the saving of all of the zinc oxide, but none of these have seemed likely to succeed commercially on account of the expensive plant required and the low value of the recovered material. It is practically impossible to get enough for the flue dust to pay for the transportation charges. Apparently the better grade of material is now lost into the atmosphere, and if this could be recovered the total product might be of higher quality.

One of the reasons for the difficulty in recovering the zinc fume is the great dilution of the flue gases, caused by opening the furnace to add to the charges in the crucibles and to work the material down into the pots. The new idea of separating solids from flue gases by means of an electrical discharge, which has been worked out by Professor Cottrell, appears to be a possible solution of this problem.

It also appears that zinc is decidedly volatile and escapes from its alloys at temperatures considerably below its boiling point. On a number of occasions white deposits, which proved on analysis to be zinc oxide, have been observed on the annealing pans. This occurred when the temperature of the heat treatment had not been above 500° C. during the operation.

It has also been frequently noted that strips of copper or copper colored alloys heated in loose contact with brass became brass colored and, in fact, that the surface of copper would be changed to brass for a depth of 0.2 to 0.3 mm. On account of these observations the following experiment was undertaken: Pieces of hard rolled brass made from 2 parts copper to 1 part zinc 2.5 cm. × 12 cm. × 0.1 cm. were wrapped in thin sheet copper and packed with fine charcoal

in a sealed copper pipe, and heated in a Sauveur furnace for one hour and for 10 hours. At 350° C. and at 450° C. there was no apparent loss. At 550° C. the loss was 0.3 gram per square meter of surface exposed in 10 hours. At 650° C. the loss was 1.5 grams per square meter in one hour and 5.4 grams per square meter in ten hours. At 750° C. it was 46 grams per square meter in one hour and 63 grams per square meter in ten hours. The copper envelope, in the heats where there was noticeable volatilization of zinc, was changed to brass on the inside surface. This means that soft brass 15 mm. thick in the usual processes of annealing in being reduced to thin sheets has lost about 1.3 per cent. of its weight, due to the volatilization of zinc. In other words, 4 per cent. of the zinc in the brass is lost by volatilization. In annealing, as it is usually carried out in the open furnace, the loss is greater on account of oxidation. Since the annealing is done at varying temperatures, it is difficult to estimate this loss, but it is probably not far from 3 per cent.

The use of chlorides as fluxes in melting promotes the volatilization of zinc. The action of vapors of common salt at temperatures considerably below the melting point of brass will completely dezincify the alloy. This is illustrated by the following experience: Brass 2.5 mm. thick was heated for one hour at approximately 650° C. in a wood-fired annealing furnace with wood which had been soaked in sea water. The result was that all but about 0.2 mm. in the center was completely dezincified, had the color of copper, and cracked apart when bent. A similar experience was had through the accidental placing in the annealing furnace of the heads and staves of an old salt barrel.

The residue and slags from the casting shops generally find their way back to the copper smelter, and, in the process of smelting, all of the zinc which these contain is lost. This loss amounts probably to a little more than 1 per cent. of the total spelter consumed in the manufacturing of wrought metals.

Taking all of these sources of loss together, it seems probable that fully 10 per cent. of the spelter used in making wrought brass is at present a total loss. In the cast brass industry, in spite of the fact that the alloys used generally contain but a small proportion of zinc, the losses must be very large on account of the use of small oil reverberatory furnaces of various types and also crucible melting furnaces which have been devised more with an idea of convenience than of preventing metallurgical losses.

DISCUSSION.

MR. PARSONS:

In order to start this discussion, I will bring out one or two points that have impressed me and I hope a good many others in the audience will have something to add. One of the first things of prime importance is to remember that most of the zinc which is mined each year is ultimately wasted. Copper, platinum, gold, or metals of that character are to a great extent stored up and accumulated and used over and over again. Probably this is less true of zinc than of any other of our important metals. For example, there are now about 59,000 tons of zinc oxide made each year and used in paint, rubber goods, and some other industries, practically none of which is ever recovered. I understand that the automobile industry is using at the present time approximately forty million pounds of zinc oxide as a filler for automobile tires.

Approximately two-thirds of all the zinc produced is used in galvanizing iron. Now that zinc, while it preserves the iron, is for the most part ultimately lost; the iron may be recovered as scrap, but little zinc is recovered from galvanized iron.

There does not seem to be much prospect of very great recovery as long as the price of zinc is low. Also in the mining of zinc there is fully as much loss as in the mining of carbon. Immense amounts of zinc are left in the ground, simply for the reason that a royalty is charged on the basis of the zinc mined and the producing companies naturally take out of the ground only that part which can be readily disposed of, and leave in the mine that which does not immediately pay them. Later the mine is covered up, filled in, and abandoned, and that part of the zinc left in the ground has little probability of ever being recovered.

Also, the peculiar chemistry of zinc—its volatility, the difficulty of its condensation when mixed with inert gases, the ease with which it reduces carbon dioxide at temperatures but little above its boiling point—makes losses in the smelting of zinc almost inevitable.

Now in the brass industry, from seven to ten per cent. of the zinc used is wasted. In Waterbury alone, there are probably 7500 pounds of zinc in the form of zinc oxide passing out of the chimneys every day. Such scrap as cannot be directly melted in the brass industry goes to a smelter in New Jersey, and if I am correctly informed as to the methods they use, the copper alone is saved. They use reverberatory furnaces with oxidizing flame, and the zinc oxide accordingly passes off into the atmosphere and is wasted.

The Geological Survey estimates that probably something like $45,000,000 of metal scrap are produced each year. These figures, as I understand them, include all scrap, both that of definite and known composition which by simple remelting can be readily used again and that of varying and unknown composition, such as is obtained through junk dealers. In the first case, there is very little waste of material, and I am personally doubtful if it should be considered "scrap" at all, for it is simply remelted to be used again in much the same way as the dough from which doughnuts are cut is again kneaded together and rolled out into sheet for further use. Even here, there is, however, a considerable loss of zinc in the remelting in crucibles, which has to be made up by the addition of more spelter. With true scrap picked up as junk the case is quite different. This is remelted in reverberating furnaces for the copper alone and the zinc passes off with the waste gases. It is impossible to accurately estimate this loss at the present time, but I know of one company that recovered 2,000,000 lbs. of copper last year from this kind of material, the corresponding zinc going to waste. The whole of this material formerly went to waste and it was some time after the waste was known before the chemist of the company could persuade the managers to let him have the necessary apparatus to recover it. It is recovered by Wifley tables, and the chemist mentioned told me that they saved $40 the first day their experimental table was installed, and $80 the second day. After that he could not buy tables fast enough to suit the management. I speak of this particularly to bring out the fact that chemists often have other problems than scientific ones to solve, namely half-hearted support from those in control, and the 17 per cent. loss mentioned by Mr. Little in the paper industry is another good example.

MR. ITTNER:

The loss in the brass industry seems to be considerable, and most of it appears to be due to volatilization and oxida-

tion. I would like to ask if it is not possible to prevent a large amount of this volatilization by simply confining the zinc during the melting process. I am not in the brass industry at all, but I have to deal with some other liquids which are more volatile than zinc, and I find that we can prevent losses by confining these liquids. If you put water in an open dish and heat it, you know that the water volatilizes; but if you confine it by a tight cover, you can heat it up to the boiling point, and over the boiling point, and not lose the water. If you want to heat it to the boiling point and do not want to have pressure, you can connect the dish with a tube, so that the pressure may be relieved.

Therefore, if zinc is lost, I would like to know why they cannot melt it in closed vessels, and if necessary to relieve any possible pressure, connect tubes with these vessels so that zinc, if it is distilled off, can be collected as metallic zinc or as oxide.

MR. DOREMUS:

A great saving of metallic zinc is effected by the substitution of dynamos for primary batteries. At the Western Union offices at the corner of Dey Street and Broadway, N. Y., there were some 30,000 primary cells in use before the introduction of dynamos. Not only was the zinc sulphate thrown away, but also most of the metallic zinc left as stubs.

A demonstration of the melting of metallic lead was given the other day in N. Y. using the "Bonecourt" system of surface combustion. The heat is applied internally. An explosive mixture of gas and air is fed, under slight pressure, into an iron pipe of $1^1/_2$ inches diameter which passes down to the bottom of the melting pot where it is united by a couple of right-angle elbows to a three-inch upright iron pipe. At the bottom of the upright pipe a plug of non-conducting material is placed, having a central hole through which the gaseous mixture passes. Broken pieces of porous contact material are placed in the three-inch pipe above the plug and the combustion of the gaseous mixture is confined to the space occupied by these pieces. The heat is applied below the surface of the molten lead and when the walls of the melting pot are suitably insulated there is great economy in the consumption of gas. The apparatus is applicable not only to the melting of lead, but also to that of type metal and other alloys.

MR. BUELL:

We have had considerable experience the last few years in trying to hold down the zinc losses and recover the oxide from the furnace gases. We have tried a good many devices and spent a good many thousand dollars without getting results which were of enough value to use, and so appreciate the desirability as well as the difficulty of the subject.

Most of the devices that have been used and suggested for recovering zinc oxide are such as are hard to use in connection with foundry work where the making of brass is the prime object, and recovery of the zinc oxide a secondary consideration.

With most of the methods, efficient modifications in the control of the furnace are necessary and this usually works to the disadvantage of the brass.

I am hoping to hear of the work which Professor Cottrell has done in regard to reclaiming such material from the chimney gases, and I agree with Mr. Bassett that this process of Professor Cottrell's promises to be a solution of the present difficulty.

MR. PRICE:

I should like to say that under the present condition of melting brass by means of coal, it would not pay to recover these zinc oxide fumes, because they are so contaminated by dirt and ashes. The only means of attacking that problem would be by means of producer gas or oil furnaces, or the solution may come some day by means of electric furnaces. I do not think it is practicable, under existing circumstances, to distil the zinc oxide fumes. You could not confine them under the operations of manufacturing practiced at the present time.

MR. ERICSON:

I am chiefly interested in the losses in zinc smelting, and it varies between 8 and 22 per cent., depending on the character of the ore. In regard to recovering zinc once used, it must be remembered that practically two-thirds of all spelter made is used in galvanizing, and consequently it covers a very large surface area, which, in connection with the cheapness of the metal, makes de-zincing impossible, such as is possible with tin, a very much higher priced metal.

In reference to electric zinc smelting, I will say that there are at present two electric zinc smelters in operation in Scandinavia, both working under the DeLaval patents, one at Trollhättan, Sweden, and the other at Sarpsborg, Norway. The cheap waterpower available makes them possible, after the technical difficulties have been overcome, and I do not believe that electrical energy generated from coal has any chance in the near future to supplant the present retort practice.

However, I have been informed that the plant at Trollhättan has contracted for 10,000 additional horsepower for enlargement. The difficulty with electric smelting with ores tried so far is that the recovery on the zinc content is so low that it can be applied only to cheap complex ores, and that a second distillation is necessary before a high-grade spelter can be obtained.

MR. GREY:

I cannot agree with the gentleman that the furnaces are not satisfactory for condensing zinc. A few years ago we had a loss of 200,000 pounds of copper out of 5,000,000. By increasing our dust chamber capacity we cut the loss down 50 per cent. You could not go below 50 per cent., because the sulphur would be converted into sulphuric acid and ruin your dust chambers. They would fall down some day after the gas was cold.

MR. PARSONS:

You will be interested to know that the Bureau of Mines is planning to take up the question of electric furnaces for these non-ferrous alloys. The problem is one of the greatest importance in the conservation of waste, for it strikes at the basis of the whole difficulty in zinc losses in alloy manufacture. The vapor pressure of pure zinc, of course, reaches atmospheric pressure at its boiling point, which Mr. Bassett has just given as about 930°. When zinc is diluted with copper, the temperature necessary for the mixture to "boil" will of course be greatly increased. Zinc losses now occur, as Mr. Ittner has indicated, simply because the melting is done in crucibles or other open containers, over which a current of air or flue gases are passing, giving every possible aid to the volatilization and oxidation of zinc. It is not at all surprising that zinc will sublime from brass under such conditions at 500° or even lower. It is exactly the same situation as the well known evaporation of water at temperatures even below its freezing point when freely exposed in open vessels. Neither zinc nor water will evaporate below their boiling point if kept in closed vessels at atmospheric pressure and of course the boiling point of zinc is raised by the addition of copper exactly as the boiling point of aqueous solutions is raised by the addition of a non-volatile solute which under certain conditions may combine with it. Accordingly, an electric furnace properly enclosed and so constructed as to overcome other difficulties, of which there are many, would be ideal. The cost of fusion would be high but other advantages, such as large units, easy stirring, low labor cost, non-intermittent firing, saving of zinc, etc., would, in my opinion, more than compensate. I personally believe that the object to be striven for is a closed furnace, and it now looks

as if this would ultimately be accomplished through the use of electricity.

MR. FLOWERS:

Another loss in zinc, which is perhaps not noticed by most chemists, is in the illustrated literature of the country, which is printed from zinc plates. As far as I know, outside of a few cents obtained for the scrap metal, the zinc consumed in etching these plates is never recovered.

MR. LANGMUIR:

It seems to me we should not only discuss the waste of zinc, but also the waste of the health and lives of the workmen from the zinc fumes.

MR. BASSETT:

It seems to me that if we can get some kind of electrically heated furnace with the electric discharge for condensing zinc fumes and obtain power cheap enough, we will be making great strides toward the end sought for.

The effect of zinc fumes on the health of the casters, in the ordinary casting shops, at least those connected with the wrought brass industry, are not any more harmful to health than is the use of tobacco. Throughout the large mills of Connecticut you will find as fine looking men engaged in casting brass as you can find in any trade where the work is carried on in intense heat. They are mostly big, husky men who enjoy life to a good old age, and do not seem to mind the effect of the zinc. Occasionally, there are men who do not seem able to stand the work, the same as in any trade where work is severe and hot, but in almost every instance the casters of brass are healthy and apparently not injured in any way by the zinc fume which, to people who are not accustomed to it, is quite troublesome. A certain zinc company in starting a new plant found great difficulty in getting help that would work in the bag room, because a considerable amount of zinc oxide was carried into the atmosphere. The laborers, who were unused to zinc, were troubled with the chills, fever and nausea that go with acute zinc poisoning, and would not stay at work until they had become accustomed to it. The company offered each man who worked a month's pay bonus. This resulted in a number staying to collect the extra pay, and as they soon became accustomed to the zinc the difficulty was overcome. The trouble with zinc is soon over and one becomes immune.

With regard to the recovery of the zinc that is distilled off, Mr. Price has answered that question fully. The brass industry has been carried on for more than a century in Connecticut. The industry was imported from England, and considerable study has been given the matter of zinc loss, but up to date we have been unable to find any way to overcome it. We hope that the work that has been done by the United States Bureau of Mines will help us.

So far as protecting the metal from the currents of air which may sweep away the zinc and produce extra volatilization is concerned, I think that this is now done thoroughly by a good heavy covering of charcoal. Of course, without the covering of charcoal, the zinc would be much more rapidly lost. The temperature at which the brass is cast, and the loss of zinc on that account, is something that we are unable to control.

I think there is no industry getting out sheet metal, wire, rods, tubes and other articles of that kind, where the perfection of the product required is as great as it is in the brass industry. The brass manufacturer, for instance, is obliged to get out brass for the maker of cartridge shells, which brass must be absolutely perfect. The practices in use in the brass mills making this material are those which have been found by experience to give a product that will meet these requirements.

NEED OF SPECIAL ALLOYS FOR SPECIAL PURPOSES.

By W. H. BASSETT.

The development in engineering construction has arrived at a point where the use of special alloys for specific requirements needs attention. These requirements may be considered under two heads: first, the physical requirements; second, resistance to corrosion.

The physical properties are easily studied in the laboratory. Machines have been devised for obtaining not only the tensile strength and elongation, but for studying hardness and resistance to abrasion and the behavior of the material under repeated stress and shock.

The matter of corrosion has been one of a more or less mysterious nature; partly, perhaps, because of a want of knowledge on the part of engineers as to the composition of the various alloys with which they deal.

Confusion has arisen on account of the names of alloys. The nomenclature used in the non-ferrous metals trade is confusing to those who are not familiar with the business. This nomenclature has, through usage, become so firmly rooted that it is practically impossible to change it. The trade names have an actual value to the producers of various material and they would naturally resist changes which would destroy such values. Years ago, Thurston undertook to introduce the name "Kalchoid" for the stronger brasses which contain a considerable percentage of zinc together with tin or iron or a combination of these elements; but as "Bronze" was a more euphonious name and represented a metal of higher cost, the trade simply paid no attention to Thurston's suggestion and to-day we have several classes of "Bronzes," *i. e.*, copper-tin alloys which are properly "Bronzes;" the copper-zinc alloys of a red color which are properly red "Brasses;" and the classes of alloys (which Thurston called "Kalchoids") which are properly Brasses containing some element or elements to give them strength and protect them from corrosion.

It would be quite evident to any chemist that accelerated corrosion at the expense of the metal containing the larger proportion of zinc will take place if two "Bronzes," one of an alloy of copper and tin and the other of the "Kalchoid" type, are placed together in an electrolyte such, for instance, as sea water. We often are asked to explain why a gun metal propeller is lost from the end of a manganese bronze shaft. It not infrequently occurs that brass strainers are held in position with copper or gun metal bolts, or a brass screen is put into position with copper rivets and burrs. Of course, galvanic action is set up in all of these cases to the destruction of the alloy containing the greater percentage of zinc. This destruction is usually brought about by the dezincification of the alloy containing the larger proportion of zinc. When this action has taken place, the material left behind is a mass of spongy copper having very little tenacity but still retaining the shape of the original material. The

brass manufacturer has many times, on account of this action, been accused of sending out his material without proper mixing. There is certainly need of more education along the line of prevention of corrosion by not putting together alloys which will naturally set up galvanic action under the conditions of exposure to which they are subjected. With iron and steel there is hardly a parallel case, but such a variety of non-ferrous alloys is possible and the composition of alloys produced by various makers for the same work so different that material of different compositions not infrequently finds its way into the same structure.

One of the best examples of the need of alloys for special purposes is that of the condenser tube problem. Condenser tubes have been made of Muntz metal having the composition of approximately 60 parts copper to 40 parts zinc and of brass having a composition of approximately two (2) parts copper to one (1) part zinc. Muntz metal is one of the alloys which may be worked hot, and is composed of mixed crystals of the α- and β-alloys. In the presence of sea water, galvanic action is started between these alloys with the result that the β-alloy becomes dezincified, leaving α-crystals in a mass of spongy copper. The action then reverses and the α-crystals are dezincified, finally leaving a tube made up of spongy and brittle copper which may be snapped off as easily as a rotten stick.

Brass tubes have proved but little better, since any substance like carbon or oxide of iron which goes into the condenser starts galvanic action with a result similar to that just described.

In order to overcome these troubles the Admiralty alloy was devised. This consists of 70 copper, 29 zinc, and 1 tin. It is much more resistant to corrosion than the alloys first mentioned as it is richer in copper and the tin exerts a protective influence. Under the conditions of exposure in polluted harbors, even this alloy will be destroyed through dezincification within a few years.

Attempts were made to obtain an alloy which would be still further resistant to corrosion, and tubes were made from alloys of copper and nickel, but these were not enough better than those from the Admiralty alloy to warrant the extra expense of production.

Attempts made to secure condenser tubes which would last by lining copper tubes with aluminum failed. Various alloys of copper, zinc and tin were tried but none of these appeared to outlast Admiralty tubes in similar service. Finally a trial has been made with a special grade of aluminum bronze, known to the trade as "Benedict Bronze," with results which indicate that this bronze is very much superior to any other alloy which has been used in condenser tubes in the presence of sea water, and especially in the presence of water in polluted harbors. Such bronzes have generally been known to be particularly resistant to corrosion, but, on account of the difficulties which were encountered in working the metals, it has not been possible to handle them with success until recently.

Another illustration of the choosing of a proper alloy for a specific purpose is shown in the failures of screens made from brass wire. A number of years ago considerable quantities of wire screens were required for houses in a tropical seaport. Brass wire screen was asked for, and furnished in 2 and 1 brass. The wire used was of fine size and when exposed to atmospheric influences would easily give way. The result of the exposure of these screens was that within a few weeks they had simply rotted and fallen to pieces. It was claimed that inferior brass had been furnished but this was not the case. Fine wire or thin sheets of alloys containing considerable zinc, when exposed to sea air or to atmospheres laden with sulphur or to ammonia fumes which arise from decomposing nitrogenous matter in the presence of dampness, are more or less rapidly disintegrated. Experienced manufacturers of fine wire cloth are aware of this difficulty, and choose only alloys which carry small amounts of zinc, *i. e.*, less than 20 per cent., these alloys not being subject to the disintegrating action of such atmospheres as we have described.

Owing to the fact that alloys have been looked upon as somewhat mysterious, there is a feeling that it is simply necessary to put together some unusual combinations to make so-called new metals which will resist corrosion or have other valuable properties. This idea, even among intelligent people, is carried to the extent that statements are accepted to the effect that fluxes can be added to molten metal which will greatly modify the properties of the castings in their resistance to corrosion or their tensile strength or other physical properties. It is safe to assert that one skilled in the art of making alloys can duplicate in every particular any alloy of which he can obtain an adequate sample, provided, of course, that he has at hand the facilities for its production.

There is beginning to be a well defined literature on the subject of alloys, and from what has already been published one can very closely predict the properties of various combinations of the more commonly known metals. For instance, Roberts-Austen, followed a number of years later by E. S. Shepherd and still later by Carpenter and Edwards, has very thoroughly covered the field of alloys of copper and zinc. The copper-tin alloys were similarly investigated by Heycock and Neville, by Shepherd and Upton, and by others. The ternary alloys of copper, tin and zinc were pretty thoroughly investigated by Thurston. An attempt to give an account of the work which has been done on the alloys of copper with aluminum, nickel, manganese and other metals would be entirely out of place at this time. There are, of course, certain particular fields which have not been very thoroughly studied, but the general properties of the alloys in these fields may be known by consulting a good metallurgical library. I simply desire to indicate that the microscope and the pyrometer have awakened new interest in the study of alloys and that

this study has now progressed to the point where one can find, by consulting a reliable authority upon the subject, data which will enable him to predict the nature of almost any alloy of which he can conceive.

DISCUSSION.

MR. PARR:

Mr. Chairman, I think it is always dangerous to talk about anything that has not yet reached the point where you are satisfied with it. However, I do not know that we are ever quite satisfied with anything we are doing, so I will venture a word as to my work on alloys.

It may not interest any one with a laboratory fund so liberal as to make it an easy matter to keep up their platinum supply to the full extent of their requirements, but the case is different with me where I have been obliged to keep actively on the job after sixteen years of almost daily service a piece of apparatus which has in its make-up some three hundred dollars worth of platinum. I refer to a Mahler bomb of the Atwater type. But more than that, instead of a single bomb to serve the needs of two or three men in investigations, and twenty-five to thirty students in class work, I want at least a half dozen. I have therefore been attempting to develop an alloy with properties as resistant to nitric and sulphuric acids as platinum.

We have reached a very satisfactory degree of success with an alloy of the nickel-chrome type having an amount of the latter constituent approximating 20 per cent. We have been able to produce quite a number of such pieces showing in $4N.HNO_3$ or $4N.H_2SO_4$, or a mixture of the above acids when preferred, a unit of 100 sq. cm. of surface and one hour of time, a solubility factor of 0.0 milligram. Other tests have shown dissolved metal to the extent of 0.09 mg., still others 0.17 mg., etc. Our greatest difficulties, however, have been met with in attempting to cast this material, the shrinkage upon solidifying being very great. With an alloy of high melting point, above 1200° C., this feature has made the case at times almost hopeless. However, we have so far succeeded that a solid cap has been cast of this material and the same has been in use for over six months on our Atwater oxygen bomb with exceedingly gratifying results.

MR. BUELL:

I should like to ask Mr. Bassett with regard to the amount of ammonia produced from the decomposition of organic material in the various localities and if it is sufficient to materially affect brass. We occasionally have cartridges returned from some of the damp warm climates such as occur around Calcutta and in the vicinity of Memphis in this country, which crack in storage from no apparent reason. These cracks are not such as would come from heat cracking or from imperfect annealing or wrong composition. I would like to know if any one has had any such experience with brass.

MR. BASSETT:

With regard to the question that Mr. Buell asked, I do not believe I know entirely as to all of the causes for this disintegration of brass. Those mentioned are some that I had had experience with. The exposure of brass articles to ammonia fumes from a dirty stable, particularly if the brass is in a hard condition, might cause it to break. An experience which I had at one time illustrates how rapidly and seriously ammonia will attack brass. A solution of copper sulphate and ammonia was mixed in a brass pail on Saturday afternoon. When the work with this solution was finished an assistant was directed to clean out the pail. He failed to do this, and on Monday morning it was noticed that the solution had begun to leak out, and the pail dropped apart between wind and water, although it was made from heavy metal. The brass in the lower section was a most perfect example of the so-called "disintegration of brass." The ammonia solution had simply rotted the alloy.

The difficulty in melting aluminum by itself, or in alloys, is its affinity for oxygen, and the failure of the oxide of aluminum to separate itself from the metal. The aluminum oxide stays in the metal, making a mess and causing all sorts of trouble. It leaves the alloy rotten and full of dirt.

MR. PRICE:

I think I can supplement these remarks of Mr. Bassett by stating a specific instance which came to my notice. We make brass acetylene generators for automobiles. We had one of these returned to us that was disintegrated. Upon investigation, it was found that the disintegration was due to ammonia salts formed with the acetylene gas when the calcium carbide was acted upon by water.

WASTE AND CONSERVATION OF POTASH AND PHOSPHORIC ACID.

By F. K. CAMERON.

As far as the phosphates are concerned, there is a great deal of waste in the Florida fields. It varies there quite a little, but sometimes amounts to as much as 200 or 300 per cent.; that is to say, for every ton of phosphate rock mined there and ground for fertilizer, twice as much phosphate rock in a comminuted condition generally is thrown away, wasted. In Tennessee, where large deposits of phosphate rock are found, the mining is very much cleaner than in Florida, and there is very little waste. The mining methods in that section have been greatly improved in recent years, and the waste is falling off. In the Charleston, S. C., fields there is still a great deal of waste.

The great problems in handling phosphates are to insist upon clean mining, and to develop methods for segregating phosphoric acid from the rock phosphate and thus make low-grade material available.

At the present time there is practically no high-grade rock, that is 72 per cent. bone phosphate, used in this country. All of the high-grade rock that we mine, or practically all of it, is shipped abroad and the American market takes only the lower-grade material. It is improbable, so far as we can judge, that there will be any very great consumption of the high-grade material in this country so long as the foreign demand keeps up, and we have to utilize the lower-grade material.

The estimates which we have been able to make from the survey of the existing fields of this country, indicate that the deposits of the high-grade rock are so large that, at three times the present rate of consumption in this country, it would last something like 1200 years; that is, excluding any new discoveries. We have not only the Florida fields, the hard rock, the pebble rock, the Charleston field, the Arkansas field, the Kentucky field and the Tennessee field, but the largest deposits of high-grade rock in the world have been discovered in Montana, Utah, Idaho and Wyoming. There are a good many fields in this country that carry some phosphorus in the rock, which makes it useful locally from the fertilizer point of view; for

instance, up in the Shenandoah Valley some rocks run two or three per cent. phosphoric acid, and some deposits are known in North Carolina, along the Piedmont Plateau, that run quite high in phosphoric acid.

The next big waste that we have to consider is the nitrogen waste. This is more or less intimately connected with carbon waste, already discussed. By the introduction of a by-product oven in this country, we are saving some of the nitrogen from the coal, as well as making gas. Both the ammonia and the gas are finding a market, but their values depend largely upon the location of the plant, and the overhead charges, which vary with the different installations. That it pays can be illustrated by the fact that one concern in a coal-mining district is taking the product from the mine, coking it, returning it to the mine owner, and paying him a royalty on it, and it is paying him very handsomely; so much so that they have made a contract for a good many years.

For press of time I can only interject here the fact that we are making in this country about one-third as much ammonium sulphate as we are importing, and what we are getting is about one-eighth as much as it is possible to make from the coal being coked at the present time.

The amount of nitrogen that is wasted in the form of fish refuse is enormous, especially on the Pacific Coast. I have seen enormous amounts of fish refuse thrown in the rivers, a perfect nuisance to the towns, washing up along the shores and banks of the rivers, and no attempt being made to utilize this most valuable material.

One of the big carbon wastes, which might have been spoken of this morning, and which contains potash, nitrogen and phosphorus, is the city wastes—the garbage and night soil. There is very little effort made to conserve these. Some doubt exists in this country as to their value as fertilizer, it being claimed by some that it is practically nil, and we are at a loss to know what the true values of these materials are. Night soil is utilized very largely in China and Japan, and some of the American gardeners in this country also use it, but there is a great objection here to its use on account of the danger from pathogenic germs. It has been found to be very good fertilizer in those countries, while in Europe and this country it has not been found to be so good. But here it has not been used under the same conditions. All of the material of this kind used in Japan and China is first worked over in appropriate pits or vessels, and "fermented" before it is applied to the field.

The biggest problem of all, for us, has been the possibility of using raw materials, waste materials if you please, for the production of potash salts. With the prospect for 1200 years of phosphates before us, we need not be very much worried at present on that score, and with the prospect of getting all the nitrogen we want from by-products of one kind and another, or by utilizing atmospheric nitrogen, bacteria, etc., we need have no serious concern on this score.

We have, however, been in a quandary as to what to use for potash, and the public mind has been very much exercised on account of the well known difficulties between this country and the one country that contains the principal source of potash for the world's supply, namely, Germany.

Now this country takes about one-fifth of the potash salts mined in Germany, and about one-half of the amount that is exported from Germany; and we had no other source of supply until quite recently. There is a possibility of our getting potash from some of the arid basins, of getting a small amount from smelter fumes, from wood ashes, and from sawdust. There is made annually in the lumber mills of this country something like 5,850,000 tons of sawdust. This is equivalent to about 5,200 tons of potassium carbonate. But when you recognize that it is scattered around the country, there is no possibility of its being of much importance for general use.

Practically all the salt wells in this country carry a small amount of potash, and when the water in the wells is evaporated, the mother liquors would give a material which compares fairly well with the so-called manure salts. It is possibly one of the waste products which could be used, but at present it will hardly pay.

Another source of potash in which people have been interested is the silicate rocks carrying potassium. There have been quite a number of processes suggested, patented or secret as the case may be, for extracting potash from silicate rock. It is possible to do so, but it is very difficult to do economically, and practically none of these processes as yet have any commercial value. There are several of them that are being tried at the present time, and some may later prove extremely valuable.

There is a silicate rock process that has given promise of becoming commercially valuable. The extraction of potash is commercially possible so long as they can get a certain by-product which, I am sorry to say, I cannot yet mention in public. This process is perfectly possible as a source of potash to the extent of 40 to 60 tons a day, but if they try to go beyond that they are certain to lose money, because they cannot get the necessary raw products, aside from the potash mineral, at figures which will enable them to make a profit. This is one of those very curious processes that the larger you make it the less it pays.

There is one substance which has been a waste product, and which has been a nuisance in that part of the country in which it grows, and that has turned out to be a very good source of potash.

Along the Pacific Coast of the United States and Alaska, there are a number of seaweeds, or kelps. In fact, we have them along the New England coast. The seaweeds have been used along the New England coast for fertilizers, and also along the coasts of the British Isles, Norway, Denmark, Sweden, the Hebrides, and have been considered extremely valuable.

Kelp rights were one of the important assets of the owners along the coasts of the countries named. But kelps have heretofore been used principally as a source of iodine, and when iodine was developed from the mother liquors of the Chile saltpeter, kelps went out of fashion and little has been thought of them until quite recently.

In examining the Pacific kelps we found that some people were interested in them as a source of iodine, and some from the standpoint of their being a nuisance. When our attention was directed to this waste matter, we were at the same time interested in potash. We organized three parties to investigate the extent of these kelp areas, mapped out the kelp beds in half of Puget Sound, and found that about 210,000 tons of the principal kelp were produced there annually; there is a great deal along the California coast from the Golden Gate down to Point Sur, and from Point Sur south there are enormous beds of very large kelps, the main kelp there being quite different from that growing in the Puget Sound region. Some of these beds, along the Southern California coast, extend from two to five miles in length and from a half to two miles in width, or even larger, and some of the large beds are extremely thick. We have mapped this past summer about one hundred square miles of kelp beds, the two principal areas being in the north, in Puget Sound, and in the south, from Point Sur southward. The plants grow in strong tideways, or where they are exposed to the full force of the open sea. All of the groves are within the three-mile limit.

We have found that the kelps in the Puget Sound area, when dried, contain as much as 30 per cent. potassium chloride and two-tenths per cent. iodine. In the South, they contain 20 to 30 per cent. potassium chloride and rather more iodine than those in the north. The kelps in the Puget Sound region (probably the same as those in Alaska) are annuals, are in best condition for cutting and have finished fruiting the latter part of July. If these kelp beds are to be a source of profit, they should be protected and should not be cut until after the middle of July. In the south, the important kelps are probably perennial and if cut not more than two feet below the surface, become as thick as before in about forty days.

It is quite impossible to give an exact estimate of the amount of potassium chloride in sight from this source. The analyses would indicate that the amount of potassium chloride to be obtained from these kelp beds annually is something like 8,000,000 tons. This is pretty big, so we are standing by a very conservative estimate of 1,000,000 tons as the probable production of potassium chloride from the Pacific kelp beds, if the beds are properly protected. This gives a source of potash at least three times as great as the total potash importations from Germany. If the larger estimates prove true, it means a possible production of potassium chloride about the same, or even a little larger than the total production in Germany.

There are all sorts of things of interest in connection with these kelps as a present waste product. It is possible to make from them a number of foods which are used in Japan and elsewhere, known as Kombus. Another series of good products is known as Nori, and while it is probable we might develop an industry in the making of these things for the Japanese, it is rather improbable that the Americans will care for them.

It is, however, probable that a cattle food might be developed in this country from kelps. The nitrogen content of these kelps would place them about the same as hay, better perhaps than the ordinary eastern hay, if not as good as the best western alfalfa; and there is a possibility that the organic material could be used as roughage for cattle food after the salts had been extracted.

It is also estimated that the possible kelp production would give us an amount of iodine, which is easily recoverable apparently, worth about $90,000,000, at present prices. These figures are possibly misleading, because the importations of iodine and iodine products, according to the figures of the Department of Commerce and Labor for the last year, would seem to be about $1,000,000 worth annually.

To put the whole matter in a nutshell, if these beds are properly protected and no longer considered a waste product but a raw product of great value, if they are properly harvested, and if we attempt seriously to utilize the iodine and other products which can be made from them, we ought to be able easily to harvest a quantity which would yield annually at least 1,000,000 tons of potassium chloride, besides vast quantities of by-products, and thus make of what has hitherto been considered a waste and a nuisance, a source of enormous commercial value.

DISCUSSION.

MR. PARSONS:

Dr. Cameron's statements with regard to iodine are especially interesting. There are many chemical substances the price of which has been held up simply because some producers prefer to obtain for certain products three times the price they could obtain if the amount was increased. The output of many of these substances can be very greatly augmented, and it has almost invariably been the case where this has been done that, although the price was diminished, new uses were found which ultimately were of great benefit to the manufacturers, and increased the profit. Many instances could be cited in chemical industry where prices have been maintained which have precluded new applications although cheaper material would mean much greater consumption. I understand an immense amount of iodine is going to waste in Chile which could be readily recovered except for the fear of reducing the price by flooding the market. It is probably true if they should increase the production of iodine, the use would be rapidly increased.

With reference to potash, there is one point which has recently come to my attention, on which I have some data which may possibly interest you. I refer to the possible use of feldspar or other potash-bearing silicates such as the green sands of New Jersey, in the manufacture of Portland cement, obtaining potash as a by-product. Now I know very well this is no new proposition and I understand that Dr. Hillebrand and Dr. Richardson applied for patents covering this idea some twenty-five years ago. Indeed some more recent patents have

been issued I think, but it is not generally known how readily potassium is volatilized in a modern cement plant.

In the cement industry there is probably anywhere from five to ten per cent. of the raw material going off in the form of dust, and that dust is becoming a menace in many parts of the country, so that cement manufacturers are beginning to realize that it is going to be to their advantage to find means for recovering it before they are required to do so. A number of experiments are under way. In one of these I happen to know that the dust, which amounts to many tons per day, carries, in the first part of the collecting flues, a considerable proportion of alkali, but further along where it is collected by the Cottrell process, it is very much richer in alkali, and some of that dust has analyzed as high as 35 per cent. soluble alkali, of which one half was potash. Now it certainly would seem that it might be possible to obtain some potash as a by-product in the cement industry, by using raw material rich in potash and making this product cover, wholly or in part, the cost of eliminating a dust nuisance. The insoluble portion of the collected dust could be returned to the kiln.

MR. SMITH:

We have been manufacturing potash from garbage in Cleveland for a long time. In the city of Cleveland, the garbage is taken care of by the city and at a profit. The material is collected every other day, put through a steam-heating process and the liquid expressed. The liquid is then evaporated and the two parts put together again, after removing the grease, and brings quite a fair price for fertilizer. The plant is operated at a profit of about $30,000 a year.

If you will come next winter at this time to Cleveland, I hope we shall be able to show you this plant in operation.

MR. HUSTON:

I am very much interested in the question, but do not know that I can add anything to this discussion. The general matter of potash supply and so on, I do not feel that I should discuss now, because there are some other important propositions that have not yet been finished, and it is not policy perhaps to make invidious remarks while those things are going on.

I was interested, however, in the remarks relative to the side products, iodine particularly. I do not know that a reduction in the price of iodine would result in a greater consumption than the reduction in the price of bromine did. This perhaps may give us some indication of what may happen in the market. As you perhaps know, the price of bromine went all to pieces and the Americans and Germans fought each other. As I heard last, the Americans were making 400 and the Germans making 300. The Americans perhaps have the best of it as their brine is richer in bromine, so the price finally came down and it is rather cheaper to run the brine into the ditch than it is to make bromine of it, and the price of bromine is probably as low as the world will ever be able to obtain it, but it has not, so far as I can learn, increased the consumption of bromine. The figures are quite worth watching, but my understanding is that it is the idea of the nitrate syndicate to make all the iodine that the world will take, but I doubt if a reduction in the price would materially increase the consumption of iodine.

MR. WHITE:

We know it is very easy to get potash from feldspar on a laboratory scale. If deposits of potash feldspar exist where it is commercially feasible to make Portland cement, it is possible as Mr. Cottrell has shown, to volatilize the potash from the cement kiln and recover it in the flue dust. It is also possible to mix feldspar with calcium carbonate and calcium chloride and by burning at a temperature of 800° C. bring the potash into soluble form. The material left after leaching might then be burned again to Portland cement. It is perhaps questionable, however, whether the process could be made to pay.

MR. BREEMAN.

The presence of potash in the dust of tubular cement furnaces, which has been referred to, is due, I think, to volatilization of potash salts. They would occur as sublimed salts like the white fumes of gunpowder (black powder) which is made up mainly of very fine solid particles of potassium carbonate. As the most volatile ingredients of the mineral substances present, these would accumulate in the dust towards the farther end of the furnace.

MR. ROBERTS

I should like to ask, Mr. Chairman, if any experiments have been made to determine the possibility of growing these Pacific Coast kelps in other waters without reducing their power of accumulating potassium?

MR. GOLDBAUM.

Russia has for a long time exported and does now export great quantities of crude potash of which the ashes from sunflower stalks furnish a considerable part. Would it be possible or feasible to raise the sunflower plant in Western U. S. and incidentally use the stalks as an auxiliary source of potash?

MR. MOORE:

There is one point in connection with these kelps which is of great interest, and that is, on drying, the larger part of the potassium chloride comes out on the surface and can be shaken off. This makes it exceedingly easy to obtain from 40 to 50 per cent. of the potash salts contained in these kelp.

MR. CAMERON:

In answer to the question about cultivating sunflower as a source of potash, there is lots of sun out there, but where there is a lack of moisture there is an additional cost to irrigate. You see the kelps do not cost anybody anything. They have the power of absorbing very much more potassium salts than any other kelps in the world. The Atlantic kelps have not as much value commercially as the Pacific kelps, on account of their absorbing a very much smaller amount of potash.

LOSSES OF COMBINED NITROGEN.

By JOHN D. PENNOCK.

Before taking up the consideration of the losses of combined nitrogen in organic substances, to which this discussion will be chiefly confined, it may be well to devote a few words to the loss of nitrogen (1) combined in inorganic substances, and (2) the loss of nitrogen in the gaseous form freed from the oxygen of the air.

Of course, the chief source of inorganic nitrogen combined in mineral form as a natural deposit is Chile saltpeter, or nitrate of soda, formed chiefly on the western coast of South America in the province of Tarapaca, Chile.

Because of the naturally restricted confines of this mineral and the comparatively small quantity known to exist (variously estimated, at the existing rate of consumption, to supply the world's demand for 50–75 years), its conservation in every way possible is a matter of exceedingly great importance.

Now, the losses of this mineral, containing 16.4 per cent. nitrogen, which is so important to agriculture as well as the arts, may come about (1) in the mining and refining of the impure mineral, called "Caliche," and (2) in the utilization of the refined product.

The "Caliche" (brown) found in the province of Tarapaca is shown by analysis[1] to be of the following composition:

	Per cent.
Sodium nitrate	60.97
Sodium iodide	0.73
Sodium chloride	16.85
Sodium sulphate	4.56
Calcium sulphate	1.33
Magnesium sulphate	5.88
Insoluble	4.06
Water	5.64

While as seen above the product as mined in Tarapaca is comparatively rich in nitrate of soda, that mined in the provinces of Pampa de Tamorugal and Atacama contains from 25 per cent. to 50 per cent. $NaNO_3$.

It is likely that in the process of refining this Caliche, which consists in lixiviating, settling or filtering, evaporation and crystallization, there is a considerable loss of the valuable $NaNO_3$. Just what this loss amounts to, the very meagre scientific information available does not enlighten us.

These deposits of nitrate are of vital importance to the world at large and, though they are held by private corporations, principally German, the Chilian government having been forced to retire from the business because of the competition of the private operators, they should be carefully conserved. Further, it might be desirable that an international committee, composed of chemists appointed by the governments of those countries most vitally interested, should visit the nitrate fields, determine what losses exist, if any, study into the present methods of refining the crude product and make recommendations for the improvement of these methods, if found unsatisfactory.

It is difficult to determine how economically the 2,251,000 tons of nitrate of soda shipped from Chile in 1910 was used. Of this, during 1910, 535,820 tons came to the United States and was used in the arts as follows:

	Per cent.
In manufacture of fertilizers	13
In manufacture of dyestuffs	12
In general chemistry	10
In glass	4
In explosives	41
In nitric acid	9
In sulphuric acid	6
Unaccounted for	5

Most of the nitrate used in dyestuffs and explosives passes through the form of nitric acid. In the manufacture of nitric acid by the ordinary method, 90–93 per cent. of the nitrogen of the nitrate is converted into nitric acid; the yield may be increased and the loss of combined nitrogen from this source reduced by the use of the Valentina vacuum process which will bring the yield to 97–98 per cent.

PURE NITROGEN.

In the early days of the manufacture of calcium cyanamide, the nitrogen necessary for the treatment of the carbide was obtained by separating nitrogen from liquid air; later the oxygen of the air was removed by passing the air over heated copper, the oxide being subsequently reduced by heating with natural gas (at Niagara Falls).

The waste gases of the precipitating towers of an ammonia soda process furnishes an abundant (2,940 tons per day in this country) supply of nitrogen which would be suitable for the manufacture of cyanamide. The oxygen of the air used to burn the coke in the lime kilns is completely converted to CO_2, so that the gas going to the precipitating towers contains only CO_2 and N, and when leaving the tower is practically pure nitrogen, there being one to two per cent. of CO_2 which could be readily absorbed by passing the gas through milk of lime. A cyanamide plant, however, is preferably located where there is cheaper power and hence cannot utilize the cheap nitrogen from an ammonia soda works.

LOSSES OF THE COMBINED NITROGEN IN ORGANIC SUBSTANCES.

The losses of the nitrogen contained in inorganic substances is unimportant compared with the losses which daily occur to the extent of hundreds of tons from the improper use of the organic substances which contain it. Further, there are many organic substances containing such high percentages of nitrogen, which at present go to waste or lie in the earth unutilized, which would produce so high a yield of ammonia that the dry distillation for ammonia alone would be very profitable. Among these substances may be mentioned shale, peat, garbage after the removal of the oils and fats, and sewage sludge. These products will yield on distillation 75–85 lbs. of ammonium sulphate per ton, or 3 times as much as coal.

Of all the losses of combined nitrogen, that which goes to waste in the manufacture of coke by the beehive process is the greatest.

In the conferences on the conservation of mineral resources inaugurated by ex-President Roosevelt a few years ago, the great loss of fuel[1] and valuable nitrogen in the beehive method of coke-making occupied a prominent part in the discussions.

James Douglas,[2] in a paper on "Conservation of Natural Resources," deplored the loss of coal and valuable by-products but stated that the development of by-product ovens could not rapidly proceed to displace the beehive ovens because chemical industry was unable to assimilate and utilize the by-products with suitable returns.

Since 1893, when the first by-product coke oven was built at Syracuse, and it was demonstrated that retort coke was equal in quality to that made in the beehive oven and the by-products, tar, ammonia, benzole and cyanides, could be recovered in sufficient quantity to make the operation a profitable one, there has been no justification for the construction of additional beehive ovens.

It is perhaps true that that particular chemical industry which converts benzole and other coal tar

[1] Machalske, *Am. Fertilizer*, **25**, 8.

[1] The easily accessible coals will be exhausted about the year 2027. M. R. Campbell and E. W. Parker, *Am. Inst. Min. Engs.*, **40**, 258.

[2] *Am. Inst. Min. Engs.*, **40**, 419.

products into colors and refined chemicals is pretty effectually fixed in the hands of Germans and not easily wrested from them, and they may continue to ship to this country seven million dollars worth of colors, but the consumption of sulphate of ammonia for fertilizers is increasing at such a rate that the United States production cannot supply the demand and nearly as much is imported as is made in this country. Further, the price is higher than it has been for several years. The same may be said of the price of tar. New uses for tar have been found so that the price has not fallen appreciably in the last ten years, although the production has increased enormously.

To what extent losses of combined nitrogen have occurred since 1893, when the retort coke ovens were introduced and the loss could have been avoided, a glance at the coke statistics will show. From 1893–1910 inclusive the coal coked in beehive ovens, where the volatile nitrogen was ruthlessly wasted in fire, amounted to about 810,000,000 tons. Had this been coked in by-product ovens, the volatile nitrogen of the coal would have yielded 23 lbs. of ammonium sulphate per ton, or a total of 9,315,000 tons, which at $60 per ton would have had a value of $558,900,000. But this would not be all. Had this ammonia been recovered, it would have been used on the soil as a fertilizer, the crops would have been increased fully 20 per cent. and the saving would have been many millions more.

PERCENTAGE OF PURE NITROGEN EVOLVED AND RECOVERED.

In the various Semet-Solvay plants throughout this country the nitrogen content of the coals varies from 1.2–1.46 per cent. The evolved nitrogen amounts to about 33 per cent. of the total contained in the coal.

Taking the results of the distillation at one of these plants, we have the distribution of the nitrogen as follows: [The nitrogen in all cases is figured to $(NH_4)_2SO_4$].

	Lbs. $(NH_4)_2SO_4$ per ton coal	
Coal, 1.3 per cent. nitrogen figured to sulphate		122.6
Ammonia yield, actual sulphate	25.0	
Nitrogen left in coke, as sulphate	78.2	
Nitrogen left in 10,000 cu. ft. gas as sulphate	12.0	
Nitrogen in tar (90 lbs. per ton) as sulphate	3.5	
Nitrogen in pyridine	0.3	
Nitrogen in cyanides	0.4	119.4
Unaccounted for		3.2

Thus the nitrogen in the coal is distributed in the various forms, as follows:

	Per cent.
Recovered as ammonia	20.3
Remaining in the coke	63.7
As elementary nitrogen in gas	8.1
In tar	2.9
As pyridine	0.25
As cyanide	0.3

Attempts have been made to increase the amount of nitrogen converted to ammonia. In cases where the ash of the coal is low, it is permissible to add lime, which must be very intimately mixed in a state of powder. The ammonia yield is increased from 10–15 per cent. If the walls of the ovens are laid up with silica brick, the lime in the coal is likely to flux with the brick and the coke will stick to the walls.

The result of a trial for five months[1] of adding 2 per cent. lime to coal carbonized in a gas works at Cheltenham, England, was an increase of 1.88 lbs. sulphate of ammonia per ton. There was an additional advantage of reducing the sulphur in the gas from 40–21.5 grains per 100 cu. ft.

METALLIC OXIDES REDUCE AMMONIA YIELD.

At one of the plants located near a blast furnace which received its supply of coke from the by-product ovens, the fine iron oxide flue dust was mixed with the coal being charged to the ovens, thinking thus to save it from the dump heap, but the effect of 3 per cent. of oxide introduced caused the NH_3 yield to fall off 8 per cent.

OTHER WAYS OF SAVING NITROGEN OF COAL.

Hundreds of thousands of tons of coal per annum are converted into producer gas in the Mond producers in England, steam being used to blow the producers and to maintain a low temperature. The gases are washed with acid and 80 lbs. of ammonium sulphate are obtained per ton of coal, four times as much as would be obtained from the same coal in a retort coke oven.

The ultimate solution of the problem of the utilization of peat will probably be the conversion to gas in a producer and the utilization of this gas in gas engines, for the handsome return from the 110 lbs. $(NH_4)_2SO_4$ saved per ton will make the proposition very profitable.

On account of the high percentage of oxygen in peat, dry distillation destroys the ammonia, but in the Mond producer, peat containing 50 per cent. moisture may be gasified, showing 75–80 per cent.[2] conversion of the nitrogen of the peat to ammonia: 4000 cu. m. of gas of 1400 calories are obtained from one ton of peat and 3–6 per cent. tar containing 15 per cent. of soft paraffin and 50 per cent. neutral oils suitable for Diesel motors.

That there is some progress toward substitution of by-product ovens for beehive is shown by the following figures: In 1900 there was total coal coked, 20,533,348 tons. In that year 1,075,727 tons were coked in by-product ovens, or 5 per cent. of the total. In 1910, of the total coke made, 41,708,810 tons, 7,138,734 tons were made in by-product ovens, or 17 per cent. This advance is encouraging. What is more encouraging is the fact that the government statistics show that a smaller number of beehive ovens were being built in 1910 than previous years and that of the total ovens, 2,567 building at the end of 1910, 1200, or 46.75 per cent., were by-product ovens. As the average coking capacity of a by-product oven is four times that of a beehive, it is evident that the additional producing capacity of 1910 was more largely by-product than beehive.

[1] *J. Soc. Chem. Ind.*, **30**, 288, 1367.
[2] *Chemiker Zeitung*, May 11, 1911, p. 505.

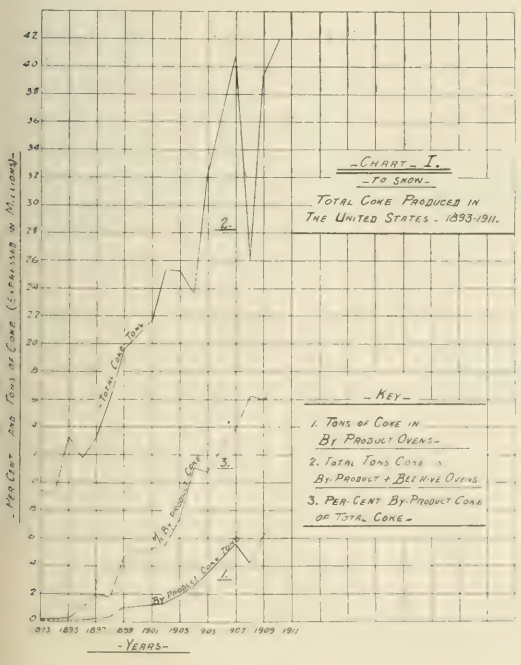
COMPARATIVE ADVANCEMENT IN SAVING OF COMBINED NITROGEN IN GERMANY, ENGLAND AND THE UNITED STATES.

When Germany began to develop the coal tar color industry she was forced to import her tar from England; the necessity for increasing the supply of tar caused Germany at once to begin abandoning the beehive ovens, substituting retort coke ovens. In 1900, 30 per cent. of the coke made in Germany was coked in retort ovens. In 1910, so complete had the transformation to retort ovens taken place that over 80 per cent. was made with recovery of ammonia and other by-products. Soon all the coal used for coke-making in Germany will be coked with the recovery of by-products. When this time arrives the retort oven will be operated for tar and ammonia as primary products and coke secondary. At such time ammonia from cyanamide or synthetic ammonia will be produced in large quantities as higher prices will make these processes profitable.

England until 1910 has been the greatest producer of sulphate of ammonia. In this year Germany nearly equaled England's production. In 1900, 10 per cent. of England's metallurgical coke was made in retort ovens; in 1910, over 18 per cent. was so made.

The retort coke output in the United States in 1900 was 5 per cent. of the total. In 1910 this had increased to 17 per cent.

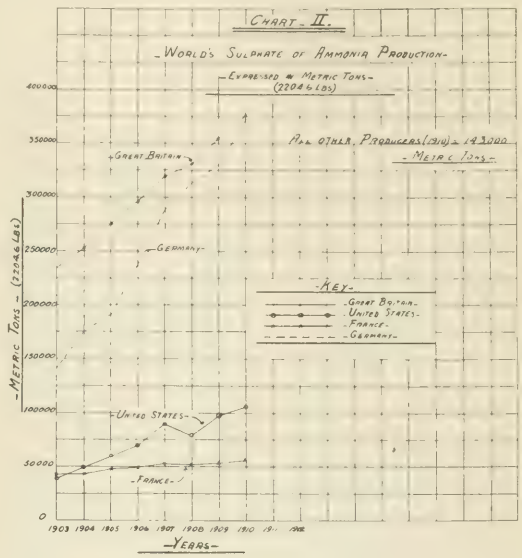
Chart I shows the increase in retort coke output year by year.



The relative standing of the four greatest producers of ammonia in the world is shown in Chart II.

Imports, domestic production, and price of ammonium sulphate are given in Chart III.

A steel manufacturer considering the expansion of his iron and steel business runs against these facts in considering by-product ovens: A beehive oven



costs about $400 and cokes 2.2 tons of coke a day; a by-product oven cokes 10 tons a day and costs, including by-product apparatus and all equipment for entire operation, $11,000–$12,000; but in spite of the greater capital invested, he can get his coke at his furnace at the same price and pay interest and depreciation on the larger investment, because of the value of the by-products obtained.

It may be shown that a corporation owning its Connellsville coal lands, and its beehive coke ovens at Connellsville, and blast furnaces and steel mills at Pittsburgh, can well afford to shut down its beehive ovens and make its coke in by-product ovens at Pittsburgh from coal shipped from Connellsville. The corporation would get its coke at the same price, taking into consideration the increased yield of coke in by-product ovens, and reducing the gross cost of the coke by the returns from tar, benzole, and part of the ammonia. In addition to supplying the coke at the same price, there will be a large part of the ammonia yield which would not be required as a credit to bring the price of the by-product coke down to the price of the beehive at Connellsville plus freight to Pittsburgh. The extra amount of ammonia is then a by-product which has cost absolutely nothing.

An important factor in reducing the cost of by-product coke is the much higher yield obtained, as stated above. The yield of Connellsville coke in by-product ovens is 73 per cent., while in beehive ovens it is 66 per cent., or 10.6 per cent. greater. Assuming this rate of increase in yield for all coal coked in beehive ovens, it may be shown that the 34,635,000 tons of coke made in beehive ovens from 52,400,000 tons of coal could have been made in by-product ovens with 47,430,000 tons; or 4,970,000

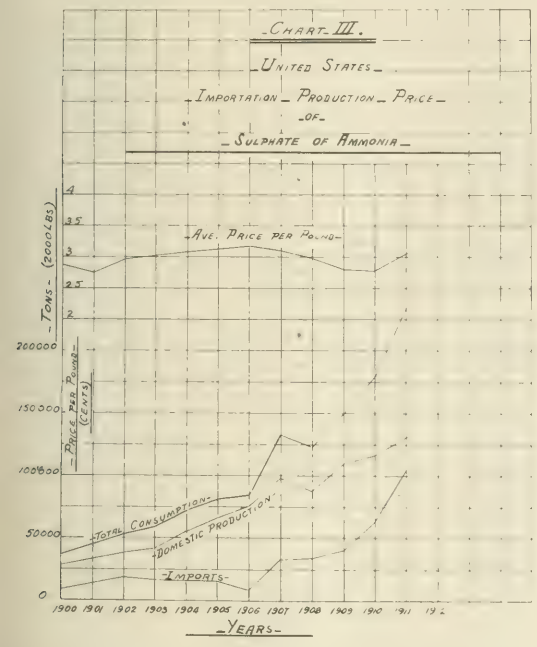
COMPLETE LIST OF BY-PRODUCT AND RETORT COKE OVEN PLANTS IN THE UNITED STATES, JANUARY 1, 1911.

SYSTEM	PLANT LOCATION	NAME OF COMPANY.	NO. OF INSTALLMENTS	DATE PUT IN OPERATION	NO. OF OVENS	USES OF COKE	USES OF SURPLUS GAS
Semet-Solvay	Ensley, Ala.	Tennessee Coal, Iron and R. R. Co.	First Second	Oct. 1898 Mar. 1902	120 120	Blast furnace	Fuel gas
"	Tuscaloosa, Ala.	Central Iron & Coal Co.	First	Feb. 1906	40	Blast furnace	Fuel gas
"	S. Chicago, Ill.	By-products Coke Corporation	First Second Third	Dec. 1905 " 1906 " 1910	120 40 40	Blast furnace, foundry and domestic.	Illuminating
"	Delray, Mich.	The Solvay Process Co.	First Second Third Fourth	Sept. 1901 Nov. 1902 Mar. 1906 " 1909	30 30 60 12	Furnace, foundry, domestic and lime-burning.	Illuminating
"	Syracuse, N. Y.	The Solvay Process Co.	First Second Third	Jan. 1893 " 1896 " 1900–1903	12 13 15	Lime-burning and foundry.	Fuel
"	Geneva, N. Y.	Empire Coke Co.	First Second	Aug. 1904 " 1909	30 16	Foundry and domestic.	Illuminating
"	Cleveland, O.	Cleveland Furnace Co.	Third	" 1910	49		
"	Dunbar, Pa.	The Dunbar Furnace Co.	First Second	" 1896 July 1903	50 60	Blast furnace.	Fuel gas
"	Chester, Pa.	Philadelphia Suburban Gas and E. Co.	First	April 1904	40	Blast furnace.	Illuminating
"	Lebanon, Pa.	Pennsylvania Steel Co.	First	July 1904	90	Furnace and gas.	Fuel and gas engines
"	Steelton, Pa.	Pennsylvania Steel Co.	First	Jan. 1907	120	Blast furnace.	Fuel gas
"	Benwood, W. Va.	National Tube Co.	First Second	Oct. 1898 Mar. 1901	60 60	Blast furnace.	Fuel gas
"	Milwaukee, Wis.	Milwaukee Coke & Gas Co.	First Second	" 1904 " 1906	80 80	Blast furnace, foundry and domestic.	Illuminating
Koppers	Woodward, Ala.	Woodward Iron Co	First	1910	60[2]	Blast furnace.	Fuel and power
"	Corey, Ala.	Tennessee Coal, Iron & R. R. Co.	First	1910	280[2]	Blast furnace.	Fuel and power
"	Joliet, Ill.	Illinois Steel Co.	First Second	1908 Mar. 1909	140 140	Blast furnace.	Fuel and power
"	Gary, Ind.	Illinois Steel Co.	First		560[2]	Blast furnace.	
United-Otto	Indianapolis, Ind.	Citizens Gas Co.	First	1909	50	Blast furnace and foundry.	Illuminating
"	Sparrows Pt., Md.	Maryland Steel Co.	First	" 1903	200	Blast furnace.	Illuminating
"	Wyandotte, Mich.	Michigan Alkali Co.	First Second	Oct. 1902 Aug. 1906	15 15	Burning limestone.	Fuel gas
"	Duluth, Minn.	Zenith Furnace Co.	First	July 1904	50	Blast furnace.	Illuminating
"	Camden, N. J.	Camden Coke Co.	Second	" 1906	50	Foundry and domestic.	Illuminating
"	Buffalo, N. Y.	Lackawanna Steel Co.	First	May 1904	564[1]	Blast furnace.	Fuel gas
"	Hamilton, O.	Hamilton Otto Coke Co.	Second	" 1909	50	Blast furnace.	Illuminating and power
"	S. Sharon, Pa.	Carnegie Steel Co.	First	July 1903	212	Blast furnace	Illuminating
"	Johnstown, Pa.	Cambria Steel Co.	Second Third Fourth	Mar. 1899 Sept. 1904 Feb. 1907	100 100 112	Blast furnace.	Fuel gas and power
Otto-Hoffman	Everett, Mass.	New England Gas & Coke Co.	First	June 1899	400	Domestic, industrial and locomotive.	Illuminating and power
"	Camden, N. J.	Camden Coke Co.	First	Jan. 1903	100	Blast furnace.	Illuminating and fuel
"	Hamilton, O.	Hamilton Otto Coke Co.	First	April 1901	50	Domestic and foundry.	Illuminating power
"	Glassport, Pa.	United Coke & Coal Co.	First	Feb 1897	120	Blast furnace and domestic	Illuminating and fuel
"	Johnstown, Pa.	Cambria Steel Co.	First	Nov. 1895	60	Blast furnace	Fuel and power
"	Lebanon, Pa	Lackawanna Iron & Steel Co.	First	Mar. 1903	232	Blast furnace	Fuel gas
Rothberg	Cleveland, O.	Cleveland Furnace Co.	Second	Oct. 1907	25	Blast furnace	Illuminating and power
"	Buffalo, N. Y.	Lackawanna Iron & Steel Co.			282	Blast furnace	Fuel gas
"	Lebanon, Pa.	Lackawanna Iron & Steel Co.	First	May 1903	5		
Didier	S. Bethlehem, Pa.	Lehigh Coke Co.	First	" 1903	300[2]		

[1] Contracted for; 188 Completed.
[2] Not completed.

tons would have been saved, would not have been mined; our mines would have been conserved to this extent and the life of the mines so much lengthened.

Further, for a ton of coal coked in by-product ovens there is gas available as fuel in the steel plant amounting to 4000–5000 cu. ft. This amount of gas is the equivalent in the steel mill of 200 lbs. of coal, or, with coal at $1.75, is worth 17.5 cts. There is, therefore, not only a saving in coal used for coking, but there would be a saving in the coal used as fuel. This would amount to 200 lbs. for every ton of coal coked in by-product ovens. We have shown above that 47,430,000 tons is the coal required in by-product ovens to take the place of the larger amount coked in 1910 in beehive ovens. Hence, the coal equivalent



for the total gas saved would be 4,743,000 tons. This added to the amount of coal saved because of higher yield of coke, we have a total saving of 9,713,000 tons of coal which could have been left in the mine in 1910 and this reduced supply of coke and coal would have been adequate for the demand.

If the Federal Government is serious in its purpose to conserve our coal resources it may do so by ruling that additional coking capacity in the future shall be of the by-product type. The average increase per annum in the past 10 years of coke production has been 2,000,000 tons. This increase would be taken care of by the building of 600 modern by-product ovens. If by-product coke is to take the place of anthracite coal for domestic fuel, as in certain places it is rapidly doing, the increase per annum will be more than 2,000,000 tons.

There seems to be among iron manufacturers, who have installed large numbers of by-product ovens, a tendency to have them in sufficient number to supply their minimum demands for coke, while the difference between the minimum and maximum is perhaps more economically supplied by beehive ovens which are a much smaller unit and may be shut down and remain idle and again started up without excessive loss or deterioration. There are in the United States 100,000 beehive ovens, 47,000 of which have been built in the last 10 years. As the life of a beehive oven is supposed to be 10–12 years, it would appear that a very large number of beehive ovens would soon be useless. Another feature of the by-product coking industry which must not escape consideration, is the increasing tendency of the illuminating gas manufacturers to look with favor upon the by-product coke oven as a valuable substitute for the small gas retort, particularly when the source of heat for coking this coal is cheap coal in a producer, for when thus operated 10,000 cu. ft. of gas is available instead of 4,500. Further, it may ultimately drive out the water gas plant, which now usually exists in illuminating gas plants to furnish 50 per cent. of the producing capacity, for its coke is of superior quality to the ordinary gas house coke and may be used for foundry purposes, and if it is sold for such purposes there will be none for the making of water gas.

It is difficult to predict the future of any industry and determine how much longer this devastating beehive coke manufacture will exist and the unnecessary loss of valuable nitrogen continue, but in the face of the crying needs of the soil, which have brought about a world's shortage of available nitrogen in spite of the placing of about 59,000 tons of cyanamide on the market, several thousand tons of Norwegian saltpeter ($CaNO_3$), a small production from the Haber process (N + H), and the very large increase in the world's production of ammonium sulphate, there will certainly be a rapid substitution of the by-product for the beehive oven. It is not unreasonable to expect that the government returns at the completion of this decade will show that 50 per cent. of the coke used in this country will come from by-product ovens; certainly the great increase in importation of ammonium sulphate in 1911, from 63,000–105,000 tons, 66 per cent., while the domestic production went from 116,000–130,000, or an increase of 12 per cent., coupled with the increase of price from 2.8 cents per lb. to 3.05 cents would warrant an expansion in the by-product coke industry.

A statement of the condition of the by-product coke industry upon Jan. 1, 1911, according to Mr. E. W. Parker, is found on the preceding page.

DISCUSSION.

MR. PARSONS:

In regard to this last paper on "Wastes of Combined Nitrogen," few realize how enormous these wastes actually are. While immense expenditures are being made in Norway in erecting furnaces to bring nitrogen into combination, we are needlessly throwing away many times as much into the atmosphere. Last year, 63,000,000 tons of bituminous coal were converted into coke containing $22,000,000 worth of nitrogen easily

recoverable as ammonium sulfate, in by-product ovens. As a matter of fact, we actually recovered but $3,800,000 worth and allowed more than $18,000,000 worth of this valuable material to go absolutely to waste. Worse even than this, over $20,000,000 worth of valuable gas and coal tar was wasted at the same time and all because this country allows the beehive coke oven to continue its ruthless career.

THE ABUSE OF BRAND.

By A. D. Little.

We all realize that a concern, which, by years of aggressive and honest advertising, has built up a reputation for quality and attached that reputation in the minds of consumers to a particular brand-name, is doing good work and that the brand itself may properly become, as it so often does, an asset of great value to the concern; and the consumer, particularly the small consumer, is very properly influenced in his selections by the reputation behind the brand-name.

On the other hand, particularly for the large consumer, and even for the small consumer, who does not stop to think very much, there is no doubt that the undue influence of the brand-name is a factor which occasions oftentimes heavy losses in the purchase of supplies.

The thing is illustrated very well by an experience that came within my knowledge a good many years ago, when a manufacturer of one of the best known brands of oilskin clothing found himself called upon to meet a pretty severe competition. His goods were known as "Fish Brand" slickers, and in certain parts of the country, notably among the fishermen, they were the kind that were given the preference always, and for which the maker and the retailer demanded a higher price. The manufacturer's method of meeting this competition was this: He had large tables in the sample rooms of his factory, and when the buyers came there, as they did at certain times of the year, and asked the price of "Fish Brand" slickers, they were told it was what it had always been. "But," they said, "we can buy slickers precisely as good as these of yours, for much less money." The manufacturer said, "I know it. Come out here," and then showed them, on a table, a great pile of his "Fish Brand" slickers, with the usual prices attached. At the other end of the table was a similar pile of slickers which he informed them were made of the same material as the "Fish Brand" in the same factory with the same care in making throughout. "You may have these slickers at the price the other manufacturers offer." "Very well," they said, "we suppose you will put the 'Fish Brand' on them." "Oh, no," he replied, "if you want 'Fish Brand' slickers you must come down to this end of the table and buy the 'Fish Brand' at the old price." And they bought the "Fish Brand" slickers, because they knew that they would meet with more ready sale, even at the higher price, by reason of the reputation which that brand had acquired with their customers.

Speaking generally, the consumer who buys by brand, instead of basing his selection on the intrinsic quality of the thing that he is buying, is pretty apt to pay a higher price.

The oil trade is one that is peculiarly given to placing a high artificial value upon the brand. I have in mind a certain oil which is very largely sold at 65 cents per gallon, that is, if you are very anxious to have that particular brand. If you are not so anxious, the price goes down to 50 and sometimes to 45 cents. But if you will take care to determine the price of oil of the same quality exactly, you will find that you can buy it in the open market at 30 cents, and sometimes as low as 27 cents per gallon. Where a man buys oil with little knowledge as to the quality, the brand-name undoubtedly helps him very much, but he often pays an inordinately high price because of his adherence to the brand.

I remember a grease sold under a certain brand, to which one concern was attached, which they purchased at 37 cents per pound. That particular grease on specification they afterward bought at 5–12 cents per pound.

The same thing is illustrated frequently in the paper mill. The paper mill superintendent is peculiarly conservative, and he also generally knows just what he wants. The trouble is that so few of them want the same thing.

The two standard brands of alum for many years have been Harrison Bros.' "Extra Concentrated" and the Natrona "Porous." Both are of excellent quality and strength and both have sold at the top of the market. Either is good enough for the best work of any mill. There are many old papermakers, however, who are convinced that it is easy to make good paper when one of these brands is used and impossible to do so with the other. As to which is which, the vote would probably be a tie.

Now the fact is, there are other alums that are quite as good as the ones bearing these brand-names, and often in the making of paper such high-grade alums are not required. Lower-grade and far cheaper alums will often serve the purpose, so that if, instead of adhering strictly to the brand-name, the superintendent had been willing to select his alum on the basis of its intrinsic properties and his particular requirements, and then buy that alum at the market price, he would have saved his employers a great deal in the course of the year. The trouble in sticking to the brand is that it narrows the range of the market, and that always means high prices.

There are a number of trade expressions that have almost the force of a brand. "Manila paper" has had for many years the reputation of being the strongest sort of wrapping paper available. The papermakers began to trade upon that reputation and upon the resistance of the consumer for paper of that name and they kept lowering the quality of such papers until today "manila paper" does not mean paper containing any manila film, but a paper made from sulphite fiber, with sometimes 60 per cent. of ground wood. At the present time there are far better wrapping papers on the market than

any of these so-called manilas. What the buyer of wrapping paper wants is area and strength. By considering these two factors in connection with price and without regard to what the paper may be called, many of the larger consumers of wrapping papers could easily save thousands of dollars a year.

"Half-and-half solder" is not half lead and half tin, but 45 per cent. lead and 55 per cent. tin, as one of our clients found upon analysis. He said to the salesman: "This is not half-and-half solder." The salesman replied: "It certainly is. If you want 50 and 50, you should have specified strictly guaranteed half-and-half."

Another example is of a cutting compound which sells at 40 cents under a brand-name and is composed of mineral oil and soap. The man who takes the trouble to find out what he is buying, who buys on intrinsic properties and money value and not on the strength of brand, saves the major portion of that amount.

There is a special sort of clay, very much favored by paper-makers. Its popularity has become so great that this clay, which originally came from a particular pit, is now in demand far beyond the capacity of that pit to supply. The result is that the operators buy up clay from a number of pits in the district and put it out under the old brand, whereas clays from these pits without the brand could probably be bought for substantially less money.

Perhaps there is no more flagrant example of the misuse of brands and the loss that comes to the consumer through buying on the name rather than the actual money value, than in the case of buying boiler compounds. We have found people buying waste molasses at 65 cents per gallon, 62 cents of which went for the brand-name, and we have found brands of boiler compounds which proved to contain only 5 per cent. of total solids, the balance being water. This situation as to certain forms of merchandise and supplies which obtains very widely in the country is very analogous to that which prevailed as to foods prior to the passage of the Pure Food Law. That law has had such far-reaching consequences for good that I am convinced that the country also needs very badly indeed a "Pure Merchandise Law." If such a law is to be secured, it must be mainly through the earnest and continued teaching and agitation of our industrial chemists.

DISCUSSION.

MR. WILLIAMS:

I am very much interested in this subject—the earnest plea for intelligent buying upon specification and the knowledge by the purchaser that he is selecting a commodity for the particular use for which it is intended, rather than buying some particular brand. We might go on and cite instances indefinitely, but one very popular error exists in the matter of the purchase of coal from a given mine. As we all know, Mother Nature did not put things down in an absolutely uniform way, and there is no good reason for expecting an absolute uniformity in the grade of coal coming from a given mine. It is very much better to use a chemist and find out the coal best suited to the particular purpose, and put it up to the dealer to get it wherever he can under the circumstances.

MR. GALLAGHER:

We received a sample of liquid some time ago which was for use with poison fly paper and vinegar and sugar. To make the fly trap thoroughly effective it was necessary to add two or three drops of the solution to the dish containing the fly paper. Careful analysis showed that the solution contained only one per cent. of sodium acetate. On our recommendation the poisoned paper, vinegar and sugar were used as specified, but without the mysterious and expensive liquid. The results, we learn, were quite as disastrous to the flies.

MR. BUELL:

One thing which works to the disadvantage of the use of specifications for these various materials and the doing away with the influence of the "Brand" is that there seem to be no definite requirements which are widely known. If it were possible to state the various properties, it would help materially and do away with a good many of the talking points which are used for maintaining the usually fictitious valuable property of any certain "Brand."

MR. PARSONS:

I had recently an interesting conversation with the Chief Chemist of one of our large oil companies on the subject of oil. He told me of the most extreme case I have ever heard, although we all know of cases where people are paying between three and four times the price they would if they bought oil instead of the brand. In the particular case cited, the salesman made the consumer believe that he should use a certain oil, at 85 cents a gallon. The buyer was a man who could be readily influenced, because about a month later another salesman told him that this man's oil was good, the very best, no doubt, but he had the same oil which he could let him have for 70 cents a gallon. And this inaugurated a rate war until the price got down to 27 cents per gallon. The oil was supplied by the refiner at 18 cents by the barrel, and was open to the public at that price if bought on specification. The fact is certainly true that automobilists are paying twice as much for the brand as they are for the oil. We are told of a case in which a man bought an oil that was said not to have any "specific gravity" in it.

MR. LITTLE:

Right along that line, I might say that the Boston School Committee some years ago bought a lot of coal which they specified as "New River coal of the best quality." When the coal came, it proved to be a low-grade Pennsylvania coal, containing something like 6 per cent. of sulphur. We presently found that it was heating up in the schoolhouses where it was stored (in one case it went up some 90 degrees in a day), making it necessary to put a gang of men to work to clean out all the coal in order to save the school-house. When the contractor appeared before the Board to explain the sudden drop in quality of New River coal, it soon developed that he did not know where New River coal originated and did not know how it came to Boston. Finally he said: "I don't know what you are kicking about anyhow. This is the same coal that you have had for the last six years."

One other case similar to that is where a concern was buying oil and had been doing so for years for 45 cents per gallon. We got out specifications for them under which the oil was offered at 23 cents; then the salesman, who sold the concern originally, came to the manager and said: "We do not want to bid on specifications; we do not believe in specifications, but you just let me know the lowest price offered on these specifications, and we will put the old brand of oil in at that price," which he did.

We had a similar case where a man who was running a laundry brought to my office a piece of material, in the form of a cube about one inch square. He had been buying it for years at

a price of 15 cents a cube and thought it was a great cleansing agent. The "manufacturer" put the price up from 15 to 25 cents a cube. This seemed too much, and he decided to investigate and see if he could not obtain the material more cheaply. The cube of material turned out to be paraffine wax weighing about 10 grams, and worth 4 cents a pound.

We had the other day a sample of coal that analyzed 4 per cent sulphur. The buyer said he did not understand the analysis at all. That the man who sold him the coal guaranteed it to be "free from sulphur and B. T. U."

THE RELATION OF THE SILICATE INDUSTRIES TO CONSERVATION.

By A. V. Bleininger.

The growth of the American silicate industries, comprising the manufactures of clay products, cement and glass, is remarkable for its steadiness. The valuation of the clay products manufactured in 1910 is estimated by the U. S. Geological Survey to have been $170,115,000, that of Portland cement $67,506,000, and the value of the various glass products for which figures are not yet available certainly cannot be less than $70,000,000. These industries are thus of a magnitude which renders them an important factor in the industrial development of the country.

The relation of the clay, cement and glass industries to conservation presents a different aspect from the one commonly considered in connection with the mineral wealth of the country. There need be no fear of exhausting the raw materials required in the manufacture of the products in question. On the contrary, their part in the policy of conservation requires that they be drawn upon on an ever increasing scale. Humanly speaking, our deposits of clay, limestone, sand, gravel, feldspar, soda, fluorspar, etc., are inexhaustible. The more of these materials enter into our civilization, the greater will be the gain of the nation inasmuch as thus more valuable materials, such as wood, are replaced and made available for more urgent needs.

The two factors entering into the manufacture of silicate products are labor and fuel. From raw materials of no intrinsic value, the hand of man fashions useful products. The interests of conservation are hence principally affected only in so far as these industries make demands upon the common fuel supply. This need not be a serious factor with proper regulation.

The silicate industries may thus be said to be valuable aids in the cause of conservation in the true sense of the word. Upon closer analysis, the functions of the clay, cement and glass products have an important bearing upon at least four important phases of modern civilization:

1. Fire proof construction.
2. Drainage, sanitation, and the control of the water resources.
3. The construction of permanent roadways.
4. Improvement of domestic and public housing conditions through the agency of a permanent architecture and the influence of the artistic handicrafts.

No chapter of our statistics is more striking than that relating to our fire losses, expressed both in terms of human life and property. It portrays realistically the policy of extravagance and recklessness which dominates our nation at the present time. Mr. Herbert M. Wilson, formerly of the U. S. Geological Survey, in an address before the National Underwriters Association in 1909, estimated the total cost of the fires, for the year 1907, excluding forest fires, but including excess cost of fire protection due to bad construction and excess premiums paid over insurance paid, at $456,485,000, "a tax upon the people exceeding the total value of the gold, silver, copper and petroleum produced in the United States in that year." The per capita loss by fire in Europe is only one-seventh of what it is in this country. Now it is evident, even to the most casual observer, that the replacement of wood as a structural material by stone, burnt clay, concrete and steel, under equitable and properly enforced building codes, would lower our fire losses tremendously. Certainly at least half of these losses are easily preventable.

An exaggerated opinion prevails as to the cost of fire-proof construction. In the case of dwellings, the cost of wood is not considerably below that of the permanent, structural materials and it has been shown in many localities that the difference does not amount to more than 10 per cent. Owing to the rapid development of the clay and cement industries on the one hand and the increasing cost of lumber on the other, it is not unlikely that the balance as regards first cost will soon be in favor of the fire-proof products. If permanency, low rate of depreciation and of repairs are considered, in addition to the fire-proof quality, this point has long been reached.

The part played by clay and concrete in the construction of our sewer and sewer disposal systems is so obvious as to need no particular mention. With reference to the sanitation of the municipal unit, the single building, a good deal remains to be done. This is especially true where aseptic conditions should prevail to as large an extent as possible, as in hospitals, school-houses, railroad stations, theaters and halls, public baths, slaughter- and packing-houses, manufactories of foods, etc. This question certainly pertains to the most important of all the conservation problems, the one dealing with public health. The clay, glass and enameled iron industries are in position to furnish us with hard, impervious, glazed surfaces, capable of being kept clean or even sterile where it is necessary. Much needs to be done yet along these lines since the sanitary conditions of thousands of our public and semi-public buildings are primitive to say the least.

As to the function of the silicate products in the work of controlling our water resources, it is scarcely necessary to say that a great part of this activity would have been utterly impossible without the enormous use of Portland cement.

One of the leading problems confronting this generation is the ubiquitous question of good roads. This need is so thoroughly realized by our citizens that any

attempt to present its economic importance, especially as related to the haulage of farm products and interurban transportation, would be unnecessary. All agree that the prevailing system of road construction and maintenance is futile and that, sooner or later, recourse must be had to permanent roads. While, in the nature of the case, native road material is to be used to as large an extent as possible, the adoption of artificial surfacing will become necessary in many cases. In the states of the Middle West, for instance, the combination of vitrified brick and concrete offers a most promising solution of the problem. The success of this kind of pavement is splendidly illustrated in Northern Ohio where, for instance, Cuyahoga County has several hundred miles of these magnificent country highways.

The fictile arts are also in position to serve the cause of a more permanent civilization by enabling the people to develop more fully the artistic aspect of our communities. This side of the question must not be underrated. The day has passed when all the energy of a vigorous people is of necessity concentrated upon the fundamental development of the country. More leisure and wealth is now available for the work of beautifying our homes, towns and cities.

There is no doubt but that the ceramic industries are rising splendidly to the occasion as is evidenced by the achievements of the terra cotta makers whose success in executing the bold designs of architects eclipses the work of the European clayworkers and the accomplishments of the wall tile and mosaic manufacturers, the makers of structural pottery, etc.

In pottery, while we have still much to learn, it is extremely gratifying to note that our production in 1910 represented a value of $33,784,000, while the imports during the same year were valued at $11,127,000. With the development of greater technical skill and especially with broader conceptions of the harmony of design and color this industry can reasonably expect to cut down the importation of European products to a very much smaller figure. The enormous increase of 99.85 per cent. in the valuation of American pottery during the last ten years entitles us to the above expectation. One factor operating against the American manufacturer is the prejudice of the public (justified in the past) in favor of the imported products, a condition which is slowly being overcome by higher standards of excellence.

Upon examining the ceramic industries from the standpoint of economy, we shall find the faults of rapid development. However, the question of the conservation of the raw materials does not enter the situation seriously. A peculiar condition prevails in the pottery industry where we find considerable quantities of raw materials, such as china clay, ball clay, and Cornish stone imported from England. This is not due to the lack of suitable materials in this country but, in part, to custom, since many of our potters are of English descent and are familiar with the excellent English clays, and, in part, to the fact that our clay resources are not as thoroughly known and appreciated as they should be. There is no question but that fine pottery can be made from native materials and, indeed, a certain amount of the clay as well as all of the feldspar and flint used are obtained from American sources. In fact, a good deal of white ware is even now being made exclusively from our own raw materials.

There is need, however, of acquainting the pottery industry with the properties of all the available native raw materials, and their correlation would be extremely desirable. This is especially true since the desire has been expressed in Europe that the export of china clay, etc., to the United States might be prohibited. Such an enactment would prove a blessing in disguise for the American potter.

The most important criticism which might be made of the ceramic industries, from the standpoint of conservation, is their reckless waste of fuel. Periodic kilns are still used most exclusively. Of six kilns examined by the writer at six plants, the one most economically operated showed an efficiency of less than 20 per cent., *i. e.*, of 100 pounds of coal used, only 20 were applied in heating the ware. This is especially objectionable where high-grade fuel, like natural gas or crude oil, is being employed. By utilizing the heat of the cooling ware and walls for drying purposes, the great fuel loss in ceramic kilns may be diminished decidedly. The use of continuous kilns, either with fixed contents and traveling fire as in the Hoffmann type, or of the tunnel kiln, with fixed furnaces and moving cars, carrying the ware, embodying the principles of recuperation and preheating would bring about a tremendous saving of fuel. Continuous kilns are used to a large extent in Europe. Thus Germany alone possesses several thousands of these kilns, and it has been estimated that their use effects a saving of from 50–70 per cent.

The Portland cement industry which formerly was conspicuous for similar extravagance has reduced the heat losses decidedly by the construction of the long rotary kilns now generally installed.

Decided improvements are still to be made as far as the glass tank and pot furnaces are concerned where regeneration or recuperation might be carried to greater development.

A large field is also open in the reduction of cost by labor-saving machinery and mechanical devices, in spite of the fact that a great deal has been accomplished. Rapid progress is being made, however, of which there are striking instances, such as the modern glass-blowing and pressing machines, the settling machines of the clay industry and many other less important devices.

By thus reducing the cost of the silicate products, the cause of conservation is promoted in a far greater degree than is generally realized.

DISCUSSION.

MR. DOREMUS:

There is a point in connection with this paper which is worth noting, in the construction of small buildings within city limits, necessarily fire-proof and within the requirements of the build-

ing laws. The building has the ordinary studding, about 4 feet apart, covered with tarred paper; over the tarred paper chicken fencing wire with open mesh is placed. On this is squirted a mixture of sand, cement and water, the mixture in one hose, and water in the other hose. It is fire-proof and, if necessary, can be made water-proof, and if you want to pull it down you can do so with a pickaxe. The walls of cement are made 1/4 inch thick on either side. The cement may be a beautiful white or gray color, and is practically impervious to moisture. The two hoses are carried around easily; the sand nozzle is lined with rubber; the sand does not affect the rubber as it does a nozzle made of steel without the rubber protection. The man stands and squirts this mixture on as you squirt with a garden hose. A square yard of surface is covered in a couple of minutes.

NEW USES TO REDUCE ABUSES IN CONSERVATION.

By W. R. Whitney.

I believe the unmodified word conservation is an unfortunate choice. To conserve is "to keep from loss, decay or injury: to preserve." Conservation is defined as the act of conserving, and to be conservative is to be "adhering to the existing order of things, opposed to change or progress." No good research chemist can afford to stop at such conservation. There is an active as there is a passive conservation; this could probably be defined as efficient utility. Considering the mineral resources of our country, we will concern ourselves with the maximum in efficient utility or be left behind. A certain well-known Corsican once said: "You cannot make an omelet without breaking an egg." There are plenty of signs that birth and growth in everything calls for the breaking of eggs and the question of efficiency is the one of interest. If you merely save your eggs, they will rot. I have collected a very few of the cases illustrating the trend of chemical work towards such active conservation.

During the past ten to twenty years, the chemists have been developing new uses for new materials very rapidly. A few years ago titaniferous iron ores were useless. Today those containing the highest proportion of titanium oxide are being mined and the ferro-titanium sold by the thousand tons. A few years ago quartz could hardly have been considered an ore. Today thousands of tons of silicon and ferro-silicon are being sold annually.

A few years ago tantalum and columbium ores were merely of interest as museum specimens. Now they are being worked for the tantalum, and doubtless the niobium will soon be utilized.

A few years ago rutile was used only in collections of minerals. It is now mined in large quantities and used in various forms in arc lamps and ought to find use in alloys.

A few years ago chromium had little use and metallic manganese was a curiosity. Now the two metals are used by the ton as pure metals in alloys for electrical resistance. They replace much greater quantities of German silver and other expensive alloys.

Ten years ago tungsten was conserved in tool steels only, while today it is saving the equivalent of millions of dollars annually in power used for lighting.

A few years ago emery was mined and was our best abrasive. Today we have artificial fused alumina and artificial carborundum, and emery is being conserved for those who later may want to see the natural material. Here, too, time and energy are being conserved with the same output of grinding.

A few years ago extensive mining operations had to be carried on to supply the graphite we use. Today that material is artificially produced from coal, which can be mined very much more economically.

It is not far back to the time when aluminum was brought into use. It now greatly helps the conservation of copper.

Poor farming land in our southern states is being worked for monazite sand, and our houses are being lighted by its use in gas mantles. This use of an ore is of our decade.

MINERAL LOSSES IN GASES AND FUMES.

By F. G. Cottrell.

In considering the mineral wastes passing out of the stacks of our smelters and metal refineries, we must distinguish clearly between the gases themselves and the clouds of suspended solid and liquid particles which they mechanically carry along with them. In which class a material belongs, often depends, to be sure, on temperature. Many metallic compounds are actually vaporized in the furnaces and gradually condense from gases into clouds of solid particles with the progressive cooling of the gas streaming through the flues. Arsenic in the form of the trioxide is usually the last of these materials to condense, since even down to 150° its vapor tension is sufficient to permit the loss, in the gaseous state, of several tons a day from the largest plants. But below, say 125° C., we may fairly consider for ordinary technical purposes that the only important element in the gaseous state is sulfur, in the form of dioxide. Detailed consideration of these losses of solids is given elsewhere in this issue of This Journal as well as in a previous article by the author[1] and still earlier by W. C. Ebaugh.[2]

For many centuries the material nature of gases and the fact that they actually possess weight escaped the chemist. Even to-day a distinct effort of mind is required to sense the vast tonnage of the clouds we see floating away so lightly from smelter and power-house stacks. There are many single stacks in this country, from each of which over five tons of gas issue per minute, while in isolated instances this is exceeded several-fold.

Aside from carbon, the element which is lost in the greatest tonnage is unquestionably sulfur. Many of our western ores will run from 25 to nearly 40 per cent. sulfur and a plant smelting 1,000 tons of ore per day is at present considered to have a very moderate capacity. The largest plants will easily touch

[1] This Journal, **3**, 543–550 (Aug., 1911).
[2] *Ibid.*, **1**, 686–689 (Oct., 1909) and **2**, 372–3 (Sept., 1910).

the 1,000 mark in tons of sulfur passing up their stacks when at full capacity. When we stop to think that this represents three times the same weight of concentrated sulfuric acid, were it made into such, and that one such plant could have supplied all the acid used in the whole phosphate industry of the United States a year ago, we can better realize the skepticism of the Smelter Companies regarding acid manufacture as a general solution of the sulfur fume problem.

The disposal of this sulfur presents unquestionably the gravest problem confronting the metallurgical industry to-day.

Suggestions have not been wanting for methods of direct absorption of this gaseous sulfur dioxide by water, limestone, lime or charcoal either as a means of final disposal or as a step in its concentration and final liquefaction under cold or pressure. One of the most ingenious and attractive is that it be used for decomposing finely granulated and moistened slag,[1] thus fixing the sulfur in harmless compounds and, at the same time, leaching out any metal values still held in the slag.

While many of these are perfectly practical on a laboratory scale, the tonnage to be handled and the cost, either in first installation or operation, have prevented them from producing any practical results up to the present.

From a chemical standpoint, the other obvious alternatives consist either in oxidation to sulfuric acid or reduction to elementary sulfur. Of these two, the first has the advantage of requiring no additional substance save the oxygen of the air, and of running itself, when properly catalyzed, without need of external energy, but unless an immediate market is at hand for the sulfuric acid, its disposal in turn becomes difficult and often impossible.

The greatest consumption of sulfuric acid in this country to-day is in the manufacture of superphosphate fertilizer, but, until very recently, the chief demand for fertilizer has been in the Southern and Atlantic States; here, too, were the chief known deposits of phosphate rock, while, on the other hand, the great smelting industry is for the most part in the far West, and cut off by high transportation costs. The recent discovery and description by the U. S. Geological Survey,[2] in Idaho, Wyoming and Montana, of what promises to be the largest phosphate deposits in the world, will, it is hoped, materially change this condition.

Much of the land in the West is still practically virgin soil; where crops are falling off, the reasons for this and their relations to different kinds of fertilizers, to tillage and crop rotation, are still so much in dispute that if we are to build a rational and permanently helpful phosphate industry, we must first have our facts well established from the standpoint of agriculture, manufacture and transportation. At present, these are not available to any extent justifying an immediate general development of the phosphate industry in the West; but coöperative work, aimed at a broad and practical study of these conditions, is already well under way between the U. S. Department of Agricultute, the Agricultural Experiment Stations of various western states, the U. S. Bureau of Mines and the large metallurgical interests of the West, and it is hoped that the results may soon justify and lead to a healthy development of the industry.

An encouraging example is before us in the work already accomplished by the Tennessee Copper Company at their plant at Copper Hill, Tennessee. They are successfully treating the weak gases from copper blast furnaces on a scale for which many predicted failure, and which certainly did require time, courage, ability and indefatigable effort to perfect. The very difficulties and delays which the work had to encounter have in one sense been a help to the industry, as their present annual capacity of 250,000 tons of chamber acid has been gradually reached over a period of some years and while it has materially reduced the price of acid in the South, the market has had a chance to adapt itself with the minimum of hardship to those already in the field and with great gain to both the metallurgical and agricultural communities.

Although much may undoubtedly be done, not only to increase the consumption of sulfuric acid in superphosphate manufacture, but also in developing other and newer uses, still we should not rest content with this.

Up to the present, we have considered only the results of oxidation of the sulfur dioxide. On the other hand, it may also be reduced to elementary sulfur, for which purpose a number of methods have been proposed, some depending on the action of solid carbon or of carbonaceous reducing gases, while others use hydrogen sulfide generated by the action of steam or acids on alkaline or metallic sulfides. An interesting general discussion both of the possibilities and the limitations of these methods together with some very suggestive new facts[1] has recently been attracting considerable attention and may not improbably lead to practical results, at least in certain special cases.

This naturally leads to the inquiry: "Why should all the sulfur of the ores be oxidized in the first place?" This question comes home still more forcibly when one looks through the charge doors of a pyritic copper blast furnace shortly after a fresh charge of ore has been dropped on the column and sees the great clouds of unburnt sulfur subliming out from the charge itself and burning above it, while all the heat thus produced is wasted.

If we could run our copper blast furnaces with gas-tight tops, as is the case with iron blast furnaces, and had full utilization of the air blown in on the lower part of the charge column, it certainly seems as though a far better thermal efficiency should be attainable, besides the possibility of delivering a very consider-

[1] "The Westby-Sorensen Process," E. P. Jenning, *Eng. and Min. Jour.*, **86**, 418–19, Aug., 1908.

[2] U. S. Geological Survey, *Bull.* **430**, "Phosphates," by H. S. Hale and R. W. Richards.

[1] "The Thiogen Process for Reduction of SO_2 in Smelter Fume," S. W. Young, *Min. and Sci. Press*, **103**, 386–387, Sept. 23, 1911.

able proportion of the sulfur of the ore to the flue in unburnt form, either as a gas or cloud of flowers of sulfur, depending on how cool the top of the ore column could be maintained.

That such a mode of operation is not entirely impossible is curiously evidenced by the fact that the first pyritic copper blast furnace ever run[1] was operated under these very conditions, the run finally terminating, after a few hours, by so much free sulfur accumulating in the flues as to stop the furnace.

In this classic article of John Hollaway's, particular stress was laid upon the recovery of the sulfur, but the development of smelting practice soon began to follow other aims. It was naturally in the hands of the copper men and sulfur did not so directly interest them. Then, too, in the far West, where pyritic smelting was first carried on successfully on the large scale and where even today probably ninety per cent. of it is still located, the limited market for sulfur and the high cost of transportation and low value per ton, as compared with copper, have naturally influenced metallurgical development to strain for the least degrees of economy in copper production, with absolute disregard for sulfur as a by-product.

In working the vast tonnage of low-grade sulfide ores of the West, effort is concentrated on burning out and slagging off the maximum amount of iron in the blast furnace in order to produce as high a percentage of copper as possible in the resulting matte, as it is much more expensive to burn out a pound of iron in the converter than it is in the blast furnace. This greater cost is due chiefly to two items, *viz.*, the cost of the refractory linings, and the greater power consumption due to the higher pressure of air in the converter. Hollaway looked on his blast furnace simply as a means of melting the ore into low-grade matte, the remaining iron of which might then be burnt off in some of the then well-known processes or in a converter which he was also the first to use in copper metallurgy.

As we have seen, it has been the cost of converter practice which has led to crowding as much of the work of oxidation upon the blast furnace as possible, and this insures the burning up of all the sulfur instead of recovering a good portion of it. Within the last few years, one of the two items of converter cost, that of linings, has been greatly reduced by the practical development of basic linings, so that to-day this factor is rapidly becoming almost negligible and all that stands in the way of shifting most of the work of oxidation from the blast furnace to the converter is the cost of the high-pressure air (10 to 15 lbs. per sq. in. as against say 3 lbs. for blast furnace) required to force its way in against the hydrostatic pressure of the deep liquid bath in the converter. If we could get a mechanically more efficient way of mixing this air with the molten matte in the converter it would mean the opening of a new chapter in metallurgy.

Even with the greater cost for air, the relation between blast furnace and converter operations is already steadily changing in the sense of taking a lower-grade matte to the converters, and this in turn may be expected to react in a study of the blast furnace from a somewhat different point of view than has hitherto obtained.

The copper blast furnace is to-day confessedly one of the crudest agencies of engineering practice, and we know with less certainty the mechanics and chemistry of its inner workings than of almost any other apparatus of equal industrial importance.

The slow development of a really fundamental scientific basis for this field of metallurgical engineering has undoubtedly been due in great part to the exceptional difficulty, if not impossibility, in this particular subject, of interpreting small scale experiments in terms of full scale operation, and the great expense of full scale experiments.

Another reason for metallurgy having lagged behind other engineering branches is perhaps to be found in the fact that commercially it has usually been pursued as an adjunct to the private ownership of some natural resource. If the mine were a rich one, the ultimate economies of smelting practice were apt to be overshadowed by the more immediately attractive study of increasing tonnage; if, on the contrary, the low grade of the ore made careful smelting necessary, the company felt it could seldom afford to go into expensive experiments for radical developments of the art, but must stay close to standard practice and make its improvements on minor details.

Even if elementary sulfur were produced its present consumption outside of sulfuric acid manufacture is too small to be at all significant, but it at last has the advantage over acid of permitting safe accumulation and storage to an unlimited extent, as illustrated by the practice in Louisiana, where it is cast into blocks some two hundred feet square and fifty feet high.

What is really most needed for the solution of the sulfur fume problem is the discovery of new uses and a wider extension of existing uses for both elementary sulfur and sulfuric acid. We have become accustomed to looking at sulfur almost exclusively from its chemical aspect, but if it is ever to be utilized in anything like the proportions in which it is now being thrown away, we would do well to consider possible mechanical uses, as, for example, a binder for sand or wood fiber. Experiments on the manufacture and use of drain tile made of such material are at present being carried out in the West where the recent rapid development of irrigation is constantly bringing new and special demands for material of construction.

If metallic sulfides are dissolved in molten sulfur, its toughness and other mechanical properties are greatly improved as first pointed out by J. B. Spence.[1] A detailed study of this form from the standpoint of structural materials has long awaited the investigator and seems much to be desired.

[1] John Hollaway. "A New Application of a Process of Rapid Oxidation by which Sulphides Are Used for Fuel." *Jour. Soc. Arts, London*, **27**, 248-270, 292-295, 488-495, 606-607, 728-730.

[1] "A New Metallic Compound" (Spence's Metal), Granville Cole, *Jour. Soc. Arts, London*, **28**, 225-229 and 279, Feb. 13, 1880. See also Thurston's "Materials of Engineering," Vol. III, p. 205.

If a sufficiently large and permanent outlet for sulfuric acid, on the one hand, and elementary sulfur on the other can be assured reasonably near the sources of supply, the metallurgical industry itself can be safely relied upon to meet the demands and find the way to supply them.

MISCELLANEOUS MINERAL WASTES.

By Chas. L. Parsons.

As the hour is so late and I have brought out a good many applications in the preceding discussion, and as a considerable portion of the subject is already in type for the February number of This Journal, under the title, "Mineral Wastes: The Chemists' Opportunity," I will present a few additional facts in the form of brief notes.

There are several kinds of waste—waste of material, waste due to inefficient methods of preparation, waste by use of unsuitable material, waste from lack of use of abundant material.

One of the great losses taking place at the present time in this country is through the destruction of valuable metals due to electrolysis induced by leakage of electric currents. The loss is difficult to estimate, but it undoubtedly means millions of dollars a year.

A good example of waste due to inefficient methods, of which there are many, is the failure to utilize modern methods in the hardening and tempering of steel. One of our large manufacturers of steel blades, making at the present time some 300,000 blades a day, has reduced their cost in the last few years, through the employment of an expert, by more than half. They use now some three tons of steel per week and the blades were formerly hardened by using sixty-five machines, utilizing gas and blast for the heating process, running day and night and requiring fifteen men for their control. This company is now using six electrically heated furnaces, giving double the capacity, in an 8-hour day, with two men doing everything. For purposes of tempering, the blades are dipped, seventy pounds at a time, into an electrically heated salt bath and held for a definite time at a temperature definitely controlled with pyrometers. Per contra, another of our largest manufacturers of small steel articles is still to my knowledge hardening each article separately by blacksmiths by hand, getting a much more variable result at many times the cost. They, too, are working up hundreds of thousands of dollars' worth of material each year. Examples illustrating this kind of waste could be almost indefinitely multiplied.

ALUMINUM.

Twenty years ago aluminum sold for five dollars a pound; today it can be bought for less than twenty cents and still is obtained only from one ore, bauxite, the deposits of which are far from inexhaustible. Bauxite has many other uses and is needed for the manufacture of alum and aluminum salts in the chemical industries. Any method for producing aluminum cheaply from clay would be of inestimable advantage. Several new patents have recently been issued, experiments are under way in this country and a prominent chemist of this Society tells me that he expects one of these processes to become a success. The methods of mining bauxite have apparently been but little studied. There are reputed to be considerable deposits in Wilkinson County, Georgia, that may pay for further exploitation. Aluminum has grown from a consumption of 83 pounds in 1883 to 47,734,000 in 1910.

ARSENIC.

According to Harkins and Swain, about thirty tons of arsenic trioxide go out of the stack of the Washoe Smelter daily. This means perhaps 80 to 90 per cent. of the total arsenic coming into the plant and amounts to over 10,000 tons a year that is being thrown out into the atmosphere from this one smelter alone. Similar losses are taking place in almost every smelting plant in the country and there is little doubt that 25,000 tons of arsenic go to waste each year. The amount recovered in 1911 increased nearly 300 per cent. over 1910, chiefly due to requirements put upon smelters for its collection. Although its price has been greatly reduced, the over-supply is not being fully taken care of. It is used in large quantities in combination with lead as an insecticide and it would seem worth while to have experiments inaugurated to determine if arsenic sulfide or calcium sulfarsenite, both of which are probably quite harmless to plants, may not be substituted as an insecticide, giving a much cheaper material, using more arsenic and conserving lead. It should be noted particularly that any proposed insecticide must be effective as a poison but must not injure the foliage of the plant upon which it is placed.

ANTIMONY.

Some losses of antimony are taking place from the flues of our smelters, but the loss is not so severe as with arsenic. Antimony lithophones are stated to have been successful in Germany, made by treating barium carbonate and antimony sulfite. The oxide itself may be used as a white paint and sodium metantimonate is a valuable constituent of enamels. Its use, however, is forbidden abroad in enamels placed on cooking utensils, but so far these enamels have not been extensively prohibited in the United States.

ASBESTOS.

The uses of asbestos are rapidly increasing and are a real conservation of lumber and a protection against fire loss. Asbestos shingles and asbestos lumber are of the utmost importance and their use should be encouraged. This country, however, produces at the present time but a very small proportion of the asbestos it uses, although very extensive deposits are known to exist in Wyoming. Anything that enables man to supplant wood with a non-combustible and cheap material is of the utmost importance to the country, for it is not only much less destructible from atmospheric agencies, but tends always to decrease our enormous fire losses.

BARITE.

Large and extensive deposits of barite occur in Missouri, Nevada and California, but transportation costs still make it possible to import more cheaply a large supply of this valuable mineral from abroad. It is used in large quantities in the production of lithophone and in paints and should at least be made to supply a goodly portion of the Western demand for this material.

BISMUTH.

The uses of bismuth are growing and if it could be obtained more cheaply, these uses would be very greatly increased. Inquiries have been recently received by the author for alloys of bismuth and lead which were needed by the ton if a low enough price could be obtained. Large quantities are being wasted in this country. Probably 3000 pounds per day are going out of the stacks of our western smelters and it is understood that one or two of our smelting companies are already installing processes for obtaining this material and placing it in greater amounts upon the American market. In 1910 nearly three-fourths of the domestic supply was imported. Bismuth is not a desirable constituent in lead and for many purposes for which lead is used the bismuth must be separated. The bismuth now produced in this country is obtained as a by-product in refining lead. The lead is melted and allowed to crystallize, the mother liquors becoming richer and richer in bismuth. Finally these mother liquors are refined electrolytically and the bismuth recovered from the slimes.

BROMINE, CHLORINE AND IODINE.

There is apparently an over-production of both bromine and chlorine in this country and new uses are desired as an outlet for these elements. Bromates are incidentally made in the production of bromides and so far have had but little market. Potassium bromate, however, is an excellent oxidizing agent and it would seem as if its use for this purpose might be greatly extended. One to two pounds of potassium bromate added to each ton of solution of potassium cyanide in the cyanide process for gold is certain to keep the bath "sweet" provided the bath is kept alkaline with lime. Any sulfides, sulfocyanides or ferrocyanides tending to reduce the value of the dissolved oxygen are apparently prevented from forming by the presence of potassium bromate.

Chlorine can now be obtained cheaply in liquid form and can be supplied either in regular cylinders, in cheap cylinders which do not need to be returned, or in tank cars if desired. Processes are also being exploited which produce the chlorine on the ground electrolytically, which, while cheapening the application, tends also to reduce the market of the works producing chlorine as a regular product. A possible use for chlorine is for chlorinating certain pyroligneous tars from wood to be used in the preservation of wood. It may be possible also to make cheap, non-combustible solvents by chlorinating certain petroleum residues like the cheap solar oil of Texas, which can now be disposed of for only about two cents a gallon. Such solvents, especially if they do not attack metals, are greatly needed. Immense quantities of chlorine in the form of calcium chloride are being run off as a waste from the ammonia soda process works of the country. One plant alone now produces 280 metric tons of calcium chloride per day, 90 per cent. of which is a total waste. Ten per cent. is, however, evaporated and used in granulated form chiefly in refrigerating plants and to be spread on roads to lay dust. This material is also found to be of very great advantage if sprinkled in coal mines, as it tends to keep the coal dust moist and thereby greatly diminishes the danger of explosions. Any non-hygroscopic substance added to water used to sprinkle coal dust in mines has little more effect than a diluent. Water itself quickly evaporates from coal dust in dry mines owing to the ventilating currents that must pass continually through these mines. If calcium chloride is added, the moisture is, of course, retained.

The price of iodine is reputed to be one that is highly artificial. It is certain that the output could be many times multiplied with little effort and the price greatly lowered if new uses could be found.

CADMIUM.

As western spelter contains an average of at least 0.3 per cent. cadmium and the production was 230,169 tons in 1910, there were, accordingly, 690 tons of cadmium sold as an impurity in zinc in that year. Cadmium is easily distilled fractionally from zinc and is an undesirable impurity. It is especially bad if the zinc is to be used for the manufacture of lithophone. Flue dust from brass works carries from about 1 1/4 per cent. to 1 1/2 per cent. cadmium, which is about 5 1/2 per cent. of the zinc actually present. On this basis there are some 400 pounds of cadmium lost each day in the flues of the brass works of Waterbury, Conn. The United States imported 4000 pounds in 1910 and produced about 5300 pounds, the price varying from sixty to seventy cents per pound. It is reported that furnaces capable of producing 1000 pounds a month are about ready to operate. New uses for cadmium are desired. At present its chief use is in glass manufacture and as a constituent of easily fusible alloys. If cheaper, it could be used extensively as a yellow pigment. It is stated that cadmium sulfide was formerly used as a yellow paint for horse cars, as it was necessary since they were kept in horse barns where hydrogen sulfide was more or less prevalent. Now that trolley cars have been substituted for horse cars the cheaper lead chromate can be used to paint cars yellow. Cadmium has also found some use as a constituent of a silver-cadmium plating alloy.

ENAMELS.

General information in regard to the preparation and constituents of enamels should be made public. They are of the utmost importance for special uses. They offer an outlet for such materials as antimony oxide, arsenic oxide, zirconium oxide, etc., and serve as a protective material conserving metals as well as greatly aiding proper sanitary conditions. They

can be sold at a very much cheaper price than at the present time. Furthermore, enamel brick and tile can be greatly improved and much of the work now done by hand can be done by machine.

FULLER'S EARTH.

The imports of English earth are regularly increasing in spite of the duty. Domestic production is still used chiefly for petroleum, while imported earth is used for edible oils. The deposits of fuller's earth in the South, especially in Georgia, South Carolina and Alabama, are almost unlimited, and there is no good reason why any foreign earth should be imported. Deposits in Arkansas and Texas are also being exploited. Domestic earth could be easily produced at a profit at one-half the present price if a sufficient output could be maintained. Several of the domestic earths bleach edible oils much better than the English. Lack of knowledge of methods of preparation for the market is one of the chief reasons why they are not now used and also some manufacturers do not yet know how to remove from edible products the slight taste these earths are apt to impart.

INFUSORIAL EARTH.

Probably the largest deposits in the world occur in Lompoc, California. The deposits there are almost inexhaustible and are remarkably free from iron and other impurities. It is used in making light terra cotta brick, in the beet sugar industry to assist in filtration and as an insulating material for covering boilers. The material in pure form has been rather hard to obtain in the past, but this immense deposit, much of which is still open to exploitation, should encourage new uses for the material.

LEAD.

Van Hise states that the losses of lead are 15 per cent. to 20 per cent. left in the mines, 15 per cent. lost in concentration and 15 per cent. to 20 per cent. lost in smelting. A large part of the lead mined is applied where it is never recovered; namely in paints and as a filler for rubber. Perhaps thirty million pounds of lead carbonate were used as a filling for rubber goods in 1910.

TIN.

There is but little tin produced in the United States, although there is distinct promise of an Alaskan supply and the output of the Texan mines is increasing. This is greatly needed, for in spite of the real conservation of the detinning recovery process, a large part of the tin produced is again lost each year.

NICKEL.

Practically all of the nickel used in the United States is imported from Canada in the form of nickel-bearing mattes and ores. Nickel is also obtained as a secondary product in the electrolyte refining of copper to the extent of a few tons annually. Large quantities of this metal are, however, known to exist in Idaho and an immense deposit of a low-grade, hydrous nickel magnesium silicate occurs at Webster, N. C. This latter deposit contains millions of tons, but owing to its low-grade character no method of economically working the material has yet been found. Of course, the same statement was true of similar ores of copper ten years ago, but these nickel ores have the disadvantage that they apparently are not amenable to ordinary methods of gravity concentration.

PETROLEUM.

Large quantities of so-called solar oils occur in the Texas petroleums, which would appear to be too good to be used for fuel but which are not light enough to be distilled for kerosene. Uses for these oils are being sought. Many million gallons of the lighter petroleum products, lying between true gasoline and natural gas, are annually lost by evaporation from the open mouths of petroleum wells and from open storage tanks.

PLATINUM AND PALLADIUM.

Owing to the craze of the rich for platinum in jewelry and its use in dentistry, the price of this metal, which is now absolutely essential to scientific research, has been trebled in recent years. One of our producing companies is now obtaining about 150 ounces of mixed platinum palladium per month which contains about 120 ounces of palladium. Platinum is being sought more and more in the West and is being conserved in the refining plants, although, as a rule, smelters do not as yet allow anything for it in ores. Every effort should be made to develop the platinum industry and to induce careful search for it and recompensation when found. The Rambler Mine, which was supposed to have run out, has apparently struck ore again. This ore formerly carried about $14 worth of platinum per ton. Palladium is used in making the dividing scales of delicate, astronomical instruments and also in jewelry. Its price per ounce is about the same as platinum but it has the advantage of lighter specific gravity. Platinum is also being conserved by the substitution of a nickel chromium alloy wire covered with platinum for the entrance wire of electric bulbs and other purposes where pure platinum was formerly used.

RADIUM.

This material is greatly desired by the medical fraternity and is important for the treatment of certain diseases. Foreign governments have taken it up, but nothing has been done in the United States, although two companies are now experimenting on its production. Large deposits of carnotite, a low-grade uranium ore, are found in Colorado, also recently in Oregon, and there is every reason to suppose that exploitation of two mines known to contain pitchblend would produce an output of this valuable, but very rare material. Our government might well take up the study of this problem both from the mining standpoint and from the producing standpoint with the hope of perfecting the methods of obtaining radium from the ore and of adding to our stocks of the material, as it is important from the standpoint of the public health. The price of radium is now about $80 per milligram of two million power. The production was 1.92 grams in 1910, which sold for about $150,000.

RARE EARTHS.

There are a large number of the rarer elements of which comparatively little is known. Even the minerals which contain them are little known and it is impossible to state how extensively they occur in the West, for they may have been overlooked as worthless. This is especially true of such elements as tungsten, vanadium, titanium, tantalum, thallium, thorium, beryllium and the twenty or more elements of the cerium and yttrium earths. No one can say what an exploitation of this field might lead to, but it is through pure scientific investigation of such problems as these that many industries have been developed, perhaps the most noteworthy recent industry being that of the Welsbach incandescent gas light. In the production of thorium from monazite by far the larger part of the associated materials goes to waste. Cerium makes up perhaps 30 per cent. of these losses. An application has recently been found in the pyrophoric alloys, which give off innumerable sparks when scratched. It is also probable that cerium oxide, lanthanum oxide and others, which occur in these waste materials, will become of special value as refractories, for they are among the most infusible materials known. Cerium is also finding a use in the form of cerium fluoride in the flaming arc and there is little doubt that these uses may be greatly extended. The properties of some of its compounds to act as perhaps the strongest oxidizing substances known may open new uses for this element. Furthermore, there appears to be a fruitful field for research in the applications of these rare elements in the production of special enamels.

REFRACTORIES.

The refractory industry offers an especially promising field of research. Many metallurgical furnaces have to be relined much more frequently than would seem to be necessary and the operation put out of commission for weeks while this relining is being carried on. A specific instance recently came to my attention where the life of the furnace was increased from six months to over two years simply by a careful study of the texture of the refractory brick used and the development of methods for decreasing their porosity. Great improvements have taken place in the last few years, but little careful scientific study has been given to the problem. Bauxite bricks offer an especially promising field if their breaking up under contraction and expansion can be controlled, which is by no means improbable. Also it is quite possible that the best fire clays can be greatly improved and brick made from them approaching bauxite brick in composition by the addition of alumina to the clay from which they are made.

SELENIUM.

Up to a year or two ago no important use for selenium was known, although for some three or four years it had been secretly used in the glass industry. It is now well known that it is used for coloring glass red and for decolorizing glass by the use of small amounts to neutralize the green of ferrous iron. It is obtained as a by-product in the refining of copper. Apparently about twenty tons per year are now utilized, which amount could be greatly increased if a larger market was found. As the price has recently been greatly reduced it is hoped that new uses will be found soon.

SULFUR.

The tremendous losses of sulfur from our western smelters has been too often dwelt on to need much additional space here. On the basis of the calculations of Harkins and Swain, the flue gases of the largest smelter in the United States are carrying off daily sulfur dioxide and sulfur trioxide, equivalent to 1,977,570 long tons of chamber acid, or more than enough to supply the total acid consumed in the whole fertilizer industry in this country. This is but a fraction of the actual sulfur wastes.

ZINC.

The immense losses of zinc have already been described in the discussion of the paper on "Zinc Losses in Brass Manufacture."

ZIRCONIA.

Zirconium oxide is important and some unworked American deposits are known. There appears to be a real field for this material as a refractory in replacing valuable tin oxide in enamels.

NEW USES.

New uses for unused material is as important in conserving mineral waste as any other one thing and there is an almost unlimited field. Calcium and silicon occur all around us by the millions of tons and can now be produced at a reasonable price if uses therefor can be found. If extensive uses were found, the prices could be greatly reduced from present cost.

Tellurium is going to waste in quantity from the copper refineries and from the plants working up gold telluride ores. Absolutely no use is now known for this material, though many tons per year could be easily obtained.

Molybdenum occurs in this country in some quantities, but no good method is known which has proved itself capable of commercially separating it from the gangue. Chemical firms have been willing to pay as high as $700 per ton for pure imported foreign material, but known uses are small. Molybdenum can replace tungsten in steel, but has the disadvantage of volatilizing out of the steel by oxidation even under the blacksmith's hammer. It is especially important in making permanent magnets and only about one-third as much is required to harden steel as when tungsten is used. It can be obtained for electrical heating purposes in the form of ribbon or wire and on account of its ductility and high melting point is used as a support for the tungsten wire in incandescent-electrical lamps.

Tungsten is finding more and more applications and with a cheapened supply will undoubtedly become one of our most important minor metals. Its use in tool steel and in incandescent lamps is rapidly increasing to the great conservation of efficiency in mechanical processes and energy in lighting.

ORIGINAL PAPERS

A NEW METHOD FOR TESTING PAINT FILMS AND PRESERVATIVE COATINGS FOR IRON AND STEEL.

By W. C. Slade.

Received Dec. 20, 1911.

In view of the difficulty in obtaining trustworthy results concerning the protective values of paints or paint films by tests conducted in the laboratory, any new laboratory method is thereby apt to be received with more or less skepticism. It is believed, however, that the method herein proposed is entirely sound in principle; and it has produced results that demand at least thoughtful consideration. It is further believed that a little more experimentation will make the method suitable for use generally. A report of the work is given at this time inasmuch as experiments related to the test have been carried on at different times for the past two or three years in the Research Laboratory of Applied Chemistry of the Massachusetts Institute of Technology, and only the very preliminary experiments have been published.

It is not intended to do the impossible in proposing a test that will at once determine the value of a paint from all points of view or under all conditions. In fact, those tests that have been used previously, or are now in general use, are all more or less limited in that they consider only certain ones of the many properties desirable in any paint film. A paint for any particular purpose should always be selected because of particular properties it possesses that other paints do not possess to the same degree. That method of testing should be used which considers most prominently those particular properties.

Unfortunately, many tests are conducted under abnormal conditions, and results thus obtained are not necessarily identical with those that would be obtained under normal or actual conditions. Thus, the Loesner steam test,[1,2] the electrical insulation or voltage test[1,2] the heat test (2 hours at 400° F.),[2] and tests where films are subjected to the action of weak acids or other attacking agents are either unnatural in themselves or are performed under unnatural conditions. Of course some of these tests are directly applicable and desirable provided the paints are to be used where steam or acid fumes prevail, or on surfaces subjected to heat, etc. Some tests eliminate the vehicle, and too often the tendency is to predict the behavior of paint films from the results of experiments carried on with the pigments contained in the films. The vehicle is too important a part of a paint to neglect. The Cushman knife blade test,[1] or Perry damp film test,[1] and the Thompson test[3] are all tests performed on the pigment alone. Nevertheless, both of these tests have produced most interesting results with commercial pigments, and it is to be noted later how closely the results, particularly of the Thompson test, agree with the results obtained by this new method. The differences noted are undoubtedly due largely to the fact that this method shows more than the Thompson method, in that it is a test for pigment and vehicle combined. It will be shown later how in certain cases the properties of a paint film may obscure the property of the pigment (as determined by the Thompson test) contained therein. One of the early tests was the evaporation test.[1,2] An iron dish painted on the inside is filled with water which is allowed to evaporate. The dish is repeatedly refilled after each evaporation until the paint film has deteriorated, or until the time of the test has extended sufficiently. From one point of view, the alternate wetting and drying periods represent the wet and dry conditions in a painted surface exposed in actual service. An acceleration test by Norton[1] involves the principle of alternate wetting and drying, but is entirely qualitative in character. The Gardner acceleration test[1] is also a qualitative one and provides for subjecting small painted test plates to artificial atmospheres. Recently, a test has been proposed by Benson and Pollock,[4] which is a sort of electrical insulation test carried out in a normal salt solution, wherein the film surfaces are subjected to a potential difference of 8 volts. There are a few other tests that have been proposed from time to time to determine specific properties of paint films such as hardness, elasticity, porosity, etc., the majority of which may be found described in the bulletins of the Paint Manufacturers' Association of the United States.

The ideal paint film would be not only uniform and tough and adhere well to the surface beneath, but would be at the same time sufficiently elastic to prevent cracking, and quite impervious to destructive gases and liquids. If it be a case of protecting iron and steel against corrosion by means of a paint film, imperviousness to moisture and to air or to oxygen is the property most essential. This new method determines the degree of imperviousness or the excluding power, and allows all results to be recorded permanently and to a certain extent quantitatively. It utilizes the principle of alternate wetting and drying, and works under conditions made to imitate actual conditions as far as possible.

DEVELOPMENT OF THE METHOD.

The method has its origin in the results of experiments with fruit-can lacquers performed by Walker and Lewis[5] in 1909, when it was shown why lacquered cans when filled with fruit juices rusted more rapidly on the inside than unlacquered cans when filled. The apparatus used was later utilized to experiment with several paint films. It consisted of a U-tube, 1″ in diameter, which contained 200 cc. normal KCl. Each arm contained a spiral of soft iron wire, one containing 25 cm. of wire, the other 100 cm., and both spirals were immersed in the electrolyte. The longer spiral bore the dried coat of paint to be tested.

The solution around the spiral was kept saturated with air by constantly bubbling a stream of air through it. The two spirals were connected through an external circuit in which was placed a bromide coulometer. An electric current developed sooner or later at the painted spiral, resulting from the depolarization of hydrogen ions by the oxygen, and the quantity of electricity developed was determined in the coulometer. The weight of bromine added per unit time may be considered as a measure of the rate of depolarization. The theory of the process will be considered more in detail later. For later reference, a few measurements obtained are given here. The films that depolarized the least head the column. The thickness of the films was not measured.

Coating.	Br. per hour, mg.
Paraffine	0.00
Zinc oxide	0.078
Graphite (baked)	0.078
White lead	0.10
Zinc chromate	0.11
Barytes	1.2
Graphite	1.87
Lampblack	2.3
Carbon black	2.4

The work was now taken up by M. T. Jones who experimented with a number of paint mixtures and used the bromide coulometer to record the various rates of depolarization. The use of the coulometer was later discontinued, however, as its resistance in the circuit during the course of a long run increased greatly, so that the quantity of electricity allowed to pass continuously fell away from that quantity which would have passed, had the resistance of the coulometer remained constant. For this reason, the results obtained with the coulometer are not given at this time. Jones next measured electromotive forces by means of the Poggendorf compensation method, but it proved too tedious and not sufficiently productive to warrant its continuance. Direct measurement of current was then attempted with the use of a specially constructed milliammeter and a few trials produced excellent results. Jones did much towards standardizing the method, and had constructed an apparatus which was at first used to allow for wetting and drying periods when his untimely death occurred. The following year the apparatus was improved and greatly extended, and the investigation continued by the writer.

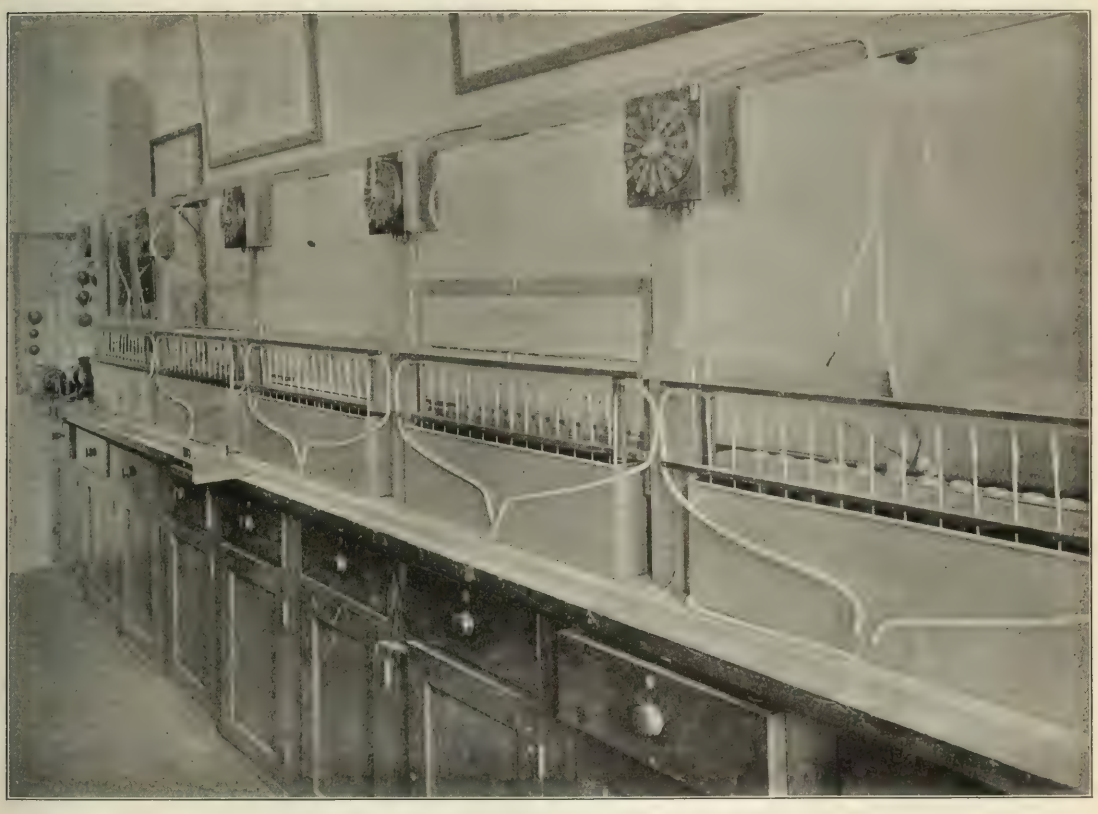
THEORY OF THE METHOD.

A brief statement of the theory of the method which involves the electrolytic theory of corrosion follows: Consider two identical pieces of iron immersed in water, containing a dissolved neutral electrolyte to give conductance, and connected through an external circuit. No current can pass through the external circuit in either direction, for identical conditions of equilibrium obtain at each metallic surface, and will obtain until this equilibrium is disturbed at one of the electrodes. By removing hydrogen ions at the surface of the electrode, as can be done by depolarizing with a steady stream of oxygen, the equilibrium can be constantly disturbed. At the same time an electric current passes continuously through the circuit. To maintain the equilibrium of ionic charges within the solution, metallic iron must pass into solution at some point in the form of ferrous ions. This takes place almost wholly at the undepolarized electrode. Of course water is the product of the depolarization, and the ferrous ions unite with the hydroxyl ions (which are chemically equivalent to those hydrogen ions removed) to form ferrous hydroxide, which in turn is oxidized to the ferric form and to insoluble rust. A rust coating forms at the depolarized electrode or cathode and so some iron must be going into solution here; but it is only a few per cent. of that moved into solution from the other electrode or anode. The cause for this probably lies almost wholly in local action on the cathode, for practically no depolarization takes place at the anode.

Let the electrodes be in the form of spirals of iron wire and the electrolyte consist of normal KCl; and consider the cathode spiral to be covered with a well dried coat of paint and the solution around it to be continuously saturated with air. The combination of painted spiral + electrolyte saturated with air—bare iron spiral + electrolyte containing no air will be called for convenience a "paint cell." The paint film may or may not electrically insulate the cathode wire. Probably every paint is porous at least to some extent, so that it is only a question of time as to how long it will require for the solution to penetrate the film sufficiently to establish contact with iron at one or more points. When this occurs, the hydrogen ions that tend to polarize are depolarized by the oxygen of the air which is in solution, and the operation of the paint cell commences. Though the driving force of the reaction is not affected by the presence of the film, the rate of reaction or depolarization is greatly affected. The initial current detected is very small—a few thousandths of a milliampere—because of the great resistance offered by the film, not only to the passage of a current but to the diffusion through the pores of the film of the air. With increased porosity comes an increased rate of diffusion and an increased rate of depolarization and a decrease in film resistance. The current consequently increases. At this time any depolarizing power possessed by linoxyn[5] that may still be unsaturated to a certain degree should show its influence. The relation between the rate of diffusion through the film and the rate of depolarization was well illustrated by an experiment where several coated spirals, with films slightly disintegrated, were supplied, first with excess air and then with excess oxygen gas. In the second instance the current values more than doubled, returning again to the original values when air was resubstituted.

The relative behavior of films made from different kinds of paints indicates the relative excluding powers to moisture and oxygen. The increase in current observed in any paint cell may be recorded in a current-time curve giving a permanent record of the behavior of the film.

It is interesting to note the analogy between the arrangement of the paint cell and the conditions existing on a painted surface, injured with scratches or bare spots, of any portion of an exposed steel structure. Assuming the injured surface to be covered with dew or rain water, then the bare spot or scratch, the protected or painted surface around the injury and the water covering both correspond respectively to the anode, cathode and electrolyte of the experimental paint cell. Of course, in this case the rate of depolarization would be less and the resistance to passage of current through the liquid circuit much greater than in case of the paint cell, but the process would proceed definitely and steadily, notwithstanding.



View of the Five Units of the Paint-Testing Apparatus.

To allow alternate wetting and drying, that actual weather conditions might be approximated, the apparatus described below was finally adopted.

THE APPARATUS.

The apparatus consists of five identical units, each unit having a testing capacity of 14 painted spirals. A view of the five units is given in one of the accompanying photographs. Each unit includes an electrolyte tank measuring approximately $28^1/_2'' \times 6^3/_4'' \times 8^1/_4''$, filled to a depth of 7″ with normal KCl solution. A metal partition with a cloth diaphragm of a width of $1^3/_4''$ along the bottom divides the tank longitudinally into two sections. The tanks and partitions are made of galvanized iron well coated on the inside with an asphaltum paint. At the back of each tank is a series of 14 tubes, closed tightly at the top with corks and wax, and extending below about 4″ into the KCl solution. Each tube contains one bare iron anode. There are also 14 cathode spirals which are held in a frame that is free to slide up and down in guides, thus permitting the spirals to be removed for periods of drying when desired. The tank is so placed that the cross-sectional dimensions of any individual paint cell is as represented in Fig. 1. A photograph of an assembled unit with the tank removed is also given.

The air is supplied by tubes held in position by a frame which can be so adjusted that each tube can deliver a stream of air bubbles directly up through a cathode spiral. This insures the continuous saturation of the solution in the immediate vicinity of the electrode. On the other hand, the anodes are so placed and so shielded from access of air (except that small amount which may diffuse down through the solution and up inside the tubes) that the oxygen content within the anode tubes is practically depleted all the time.

Each cathode is connected to its corresponding

anode through an external circuit. The connections are all made in a switch-box, shown in the photographs, in such a manner that when the paint cells are working, each cell sends its current through an individual 100-ohm resistance coil; and when measurements are to be made, and a milliammeter with an internal resistance of 100 ohms has been connected to the binding posts of the box, then, by moving a radial contact arm, the current from any individual paint cell may be sent at once through the 100-ohm coil of the milliammeter instead of through its 100-ohm coil in the switch-box. Each paint cell is entirely distinct from its neighbors. The fourteen paint cells have only the electrolyte in common. The use of the resistance coils makes it possible to read

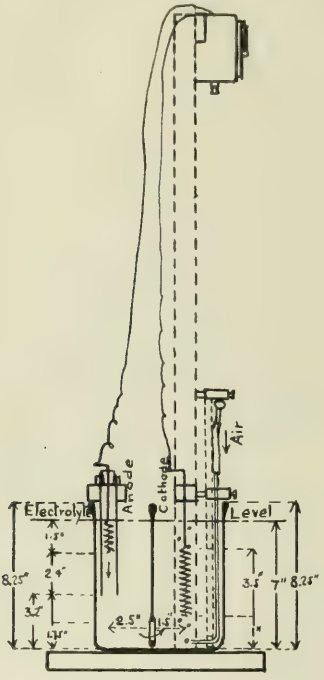


FIG I
Cross-section "Paint-cell" No. I.

directly the current that is actually passing when the milliammeter is thrown into circuit.

The resistance coils are made of No. 36 German silver wire and are wound on glass tubes which in turn are inserted into small 3" weighing tubes closed at the end with sealing-wax. They were checked against a standard when made and are correct to within $^1/_5$ per cent.

The air, supplied by a small motor-driven rotary blower (E), passes first into an equalizing chamber and then into the main distributing pipe. The supply is steady and regulated to about $^1/_8$–$^1/_4$ cu. ft. per minute per tank.

The wetting and drying periods are controlled by clock work. The hour hand of the clock (C) makes contacts at desired intervals such that electric circuits are made. A relay is thereby brought into play and a larger current passes through a motor (B) which controls the raising and lowering mechanism

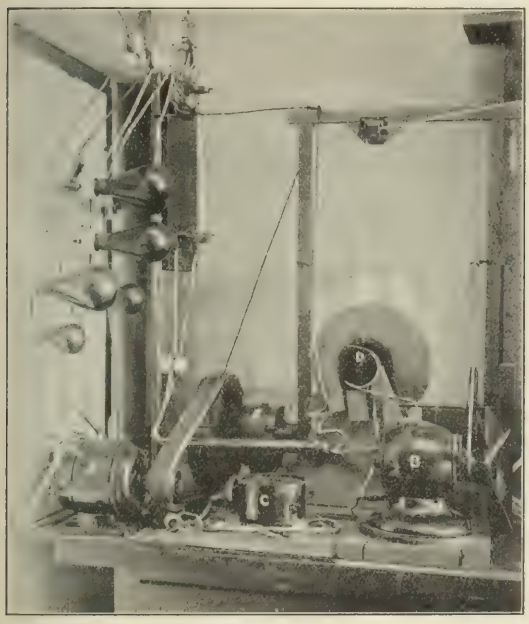
of the cathode frames. According to the particular contact that the hour hand makes, the frames are raised or lowered. For tests recorded in this paper, the wiring was arranged to give lifting contacts at 3, 6, 9 and 12 o'clock and lowering contacts at 1, 4, 7 and 10 o'clock. There were thus 8 one-hour drying periods and 8 two-hour wetting periods per 24 hours.

The spirals are made of a soft iron wire, No. 19, U. S. standard, and wound in a lathe on a $^3/_4$" lag screw having $4^2/_3$ threads per inch. The electrodes are so wound that when in proper position exactly 100 cm. of the cathode wire and 25 cm. of the anode wire is under the solution. All spirals are cleaned by pickling in dilute sulphuric acid. They are then carefully washed with water and dried with alcohol or ether.

CONCERNING THE PAINTS AND PAINT FILMS TESTED.

To determine as far as possible the value of the apparatus, paint mixtures were made from ten rep-

resentative commercial pigments, some of which are recognized as good, and some as poor paints, according to the point of view. The pigments were kindly furnished by the Paint Manufacturers' Association and came in paste form, ground in pure, refined linseed oil. In each case they were thinned to the desired viscosity with a mixture by volume of $^2/_3$ pure raw oil and $^1/_3$ oil of turpentine. The amount of oil used in grinding each pigment, and the amount of vehicle used for thinning each, is on record. The object was to obtain a fairly rapidly drying paint mixture that would be of a viscosity not far from that desired for practical application, and at the same time be of such a nature that fairly thick and very uniform coats could be obtained on the iron spirals. Herein lay a difficulty. The paints investigated were zinc oxide, zinc-lead chromate, American vermilion, red lead, white lead, iron oxide, barytes,



silica, carbon black and natural graphite. Now the fineness of a pigment determines the thickness of the paint film. Whether or not the various mixtures were of comparable viscosities, several of the paints when applied in coats at all thick tended to slide off from the wire. This was the case with the paint made from some of the more coarsely ground pigments. The difficulty was obviated to a great extent, however, by the method of drying the films.

The carefully cleaned cathode spirals were coated by dipping into the well shaken paint mixture. The excess paint was allowed to drain until dropping began and the spirals then transferred to a drying wheel. This consisted of a wooden wheel about two feet in diameter, slowly rotating in a vertical plane. Its face was divided by partitions into eight compartments, each compartment enclosing a number of holes drilled into the face of the wheel. The ends of the coated spirals were inserted into the holes in such fashion that the spirals turned with the wheel, thus permitting the fresh paint to flow around the wire rather than drain away in drops. Eight different paints could be dried at one time. When sufficiently tacky, the spirals were transferred to a window with western exposure for thorough drying.

The magnitude of the variations in thickness of the films can be best represented by giving a few measurements made by calipering two coat films. The coats as a rule were fairly uniform, but variations up to 20 per cent. occurred at some places.

	Paint.	Average thickness. (Several readings.) Test I. mm.	Test II. mm.
3	American vermilion	0.09	0.09
7	Barytes	0.09	0.09
4	Red lead	0.10	0.09
5	White lead	0.10	0.08
6	Iron oxide	0.10	0.07
8	Silica	0.10	0.09
9	Carbon black	0.13	0.12
1	Zinc oxide	0.14	
2	Zinc-lead chromate	0.14	..
10	Graphite	0.14	..

When spirals were given a single coat, the time for drying varied from 2–3 weeks. In case of two coats of paint, the first coat dried 3 or 4 days and the second coat 2–3 weeks, except that films in the first series dried about a month.

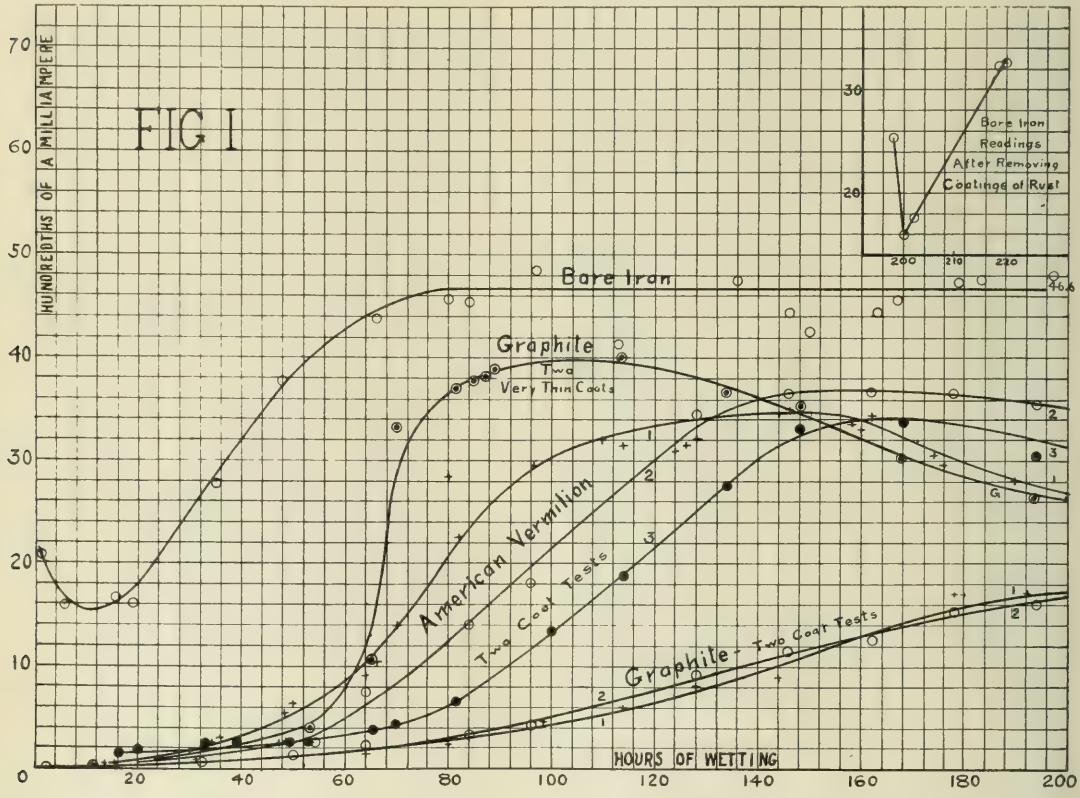
METHOD OF TESTING AND TREATMENT OF DATA.

For each separate paint test three spirals are coated simultaneously and dried for the same period of time. They are then properly adjusted in the cathode frame and connections from the switch-box made by soldering. Air is then bubbled through the solution, and at the proper time the first immersion begun. Current readings are taken at the start and after this at the end of each two-hour wetting period. Unless one value chances to be considerably in error, the three readings are averaged. It is this average that determines a point for a current-time curve, one of which is drawn for each test, and which is so drawn as to be the most representative curve. Most of the tests were extended over a period of 300 hours of wetting, but it appears that 200 hours, and perhaps even 150 hours, is quite sufficient. The thickness of a coat or the number of coats really determines the time required. On Plots I and II are given several curves together with the experimentally determined points.

With each one of the ten paint mixtures two one-coat tests and three two-coat tests were carried out, excepting zinc-lead chromate, zinc oxide and graphite, where only two two-coat tests were finished. From the curves determined as described above, in only one case, the one-coat tests with white lead, was there wide divergence between the two curves; with the exception of a few cases of only fair agreement, the several runs checked up very well. Referring to Plots I and II, the curves for all the paints but

American vermilion are examples of the generally good agreement obtained. The character of the checks among the American vermilion curves is typical of the less accurate checks obtained in the cases of only fair agreement, such as the two-coat tests of red lead, white lead and iron oxide. It was almost impossible to get a good, uniform coating of white lead of the desired thickness—such that it would be comparable with the thickness of the other films. To this fact may be traced the cause of the great disagreement between the white lead tests, and the smaller disagreements in a few of the other tests. On the whole, all the paints considered, the several runs check among themselves very well. The spirals for the several series of tests were coated and dried at different times, with the periods of drying varying somewhat, necessitated by the lack of time. Besides, the several series of tests were carried out in different tanks and at different times, thus giving all opportunity for disturbing factors to appear. It is impossible to include all the preliminary curves because of the space required.

In order to bring the results together in comparative relationship, Plots III and IV have been prepared. Each curve on both of these plots is drawn from data obtained from the various best representative curves of the individual tests by averaging these curves. Each curve on Plot III is determined by the position of two of the one-coat test curves; those on Plot IV by the positions of the three corresponding two-coat test curves. Both sets of curves are discussed later. It may be noted here, however, that the increased protection of the two coats over the one coat of each paint shows up well; also that the relative position of the curves on both plots is in general the same. It will be remembered that the films of zinc oxide, zinc-lead chromate, carbon black and graphite were slightly thicker than the other films. But the difference is only great enough to account for but a small part of the wide divergence from one another of the finally determined mean curves. Aside from influence of thickness, which is directly related to excluding power, is to be considered the influence of the depolarizing property of the film



It appears that this is more a property of the film as a whole, than a property of any constituent part of the film. Both factors are to be considered more fully.

INTERPRETATION OF THE CURRENT-TIME CURVES.

On Plots I, III and IV appears a curve called the bare iron curve. This was determined by making a run with fourteen carefully cleaned bare iron cathodes exactly similar to those used in the paint tests. The points locating the curve are shown on Plot I. At the start of the test with no rust on the spirals the current was about 0.20 milliampere. As a thin rust film formed, either the resistance must

have increased or the electromotive force decreased, for at 10 hours of wetting a minimum value of about 0.16 milliampere was reached. Beyond this point the current rapidly increased until a constant value of 0.466 milliampere was reached. This period of increase marks also the period of rapid accumulation of a rust coating. At the end of 197 hours of wetting, the accumulated rust, which acted as a spongy envelope about the wire, was carefully removed, and the run again continued. The current immediately fell to about 0.25 milliampere and, as previously, strangely enough passed through a minimum before rust formation caused another rise. The increase in current was concomitant with the

Evidently there are two distinct effects that tend to overshadow each other: that of depolarization, which is most pronounced in thin coats that disintegrate easily (and so acquire high powers of absorption), and the effect of exclusion or imperviousness, which increases as the thickness of any coat or the number of coats is increased.

It is interesting to note that zinc oxide, zinc-lead chromate, carbon black and graphite appear as the best excluders. But given a film sufficiently thin, such that the depolarizing effect may become prominent, then it is again to be noted that while zinc oxide and zinc-lead chromate do not increase the rate of depolarization, carbon black and graphite

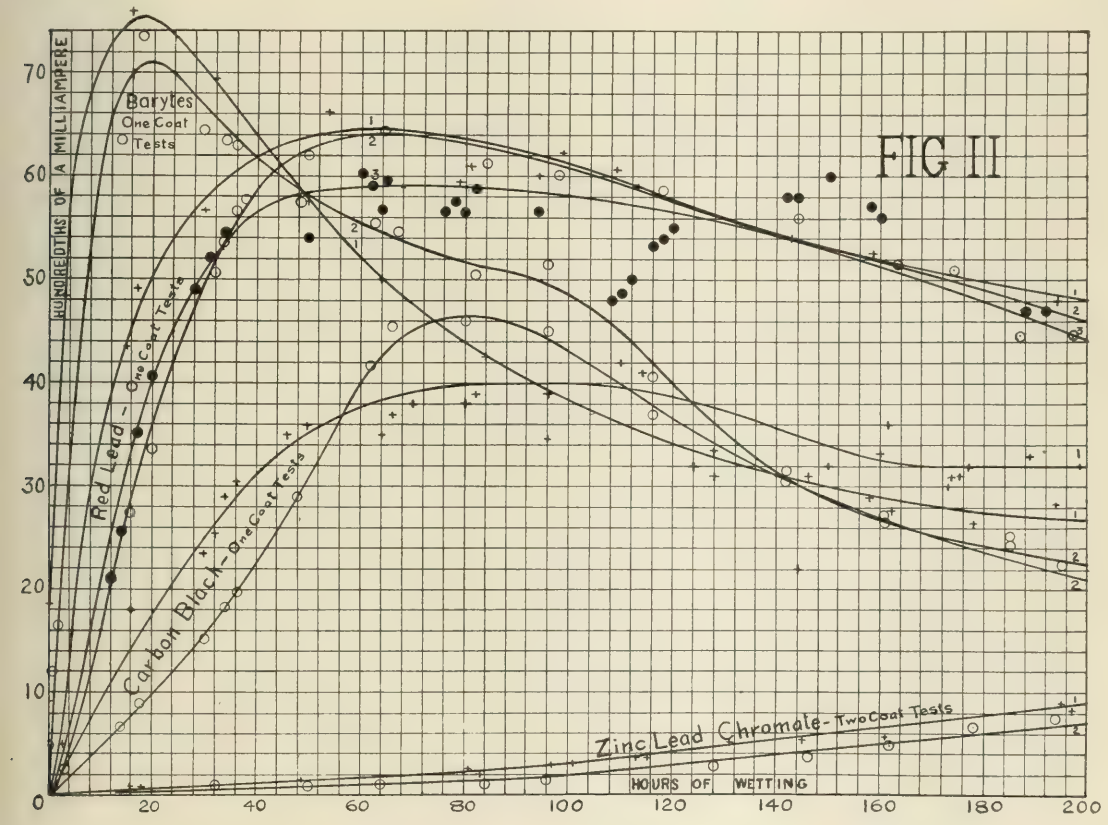


FIG II

increase in depolarizing power of the coating. Within the spongy envelope the rate of the union of hydrogen and oxygen was increased. For the first few hours of wetting, the quantity of rust formed is not sufficient to exert its influence in this direction.

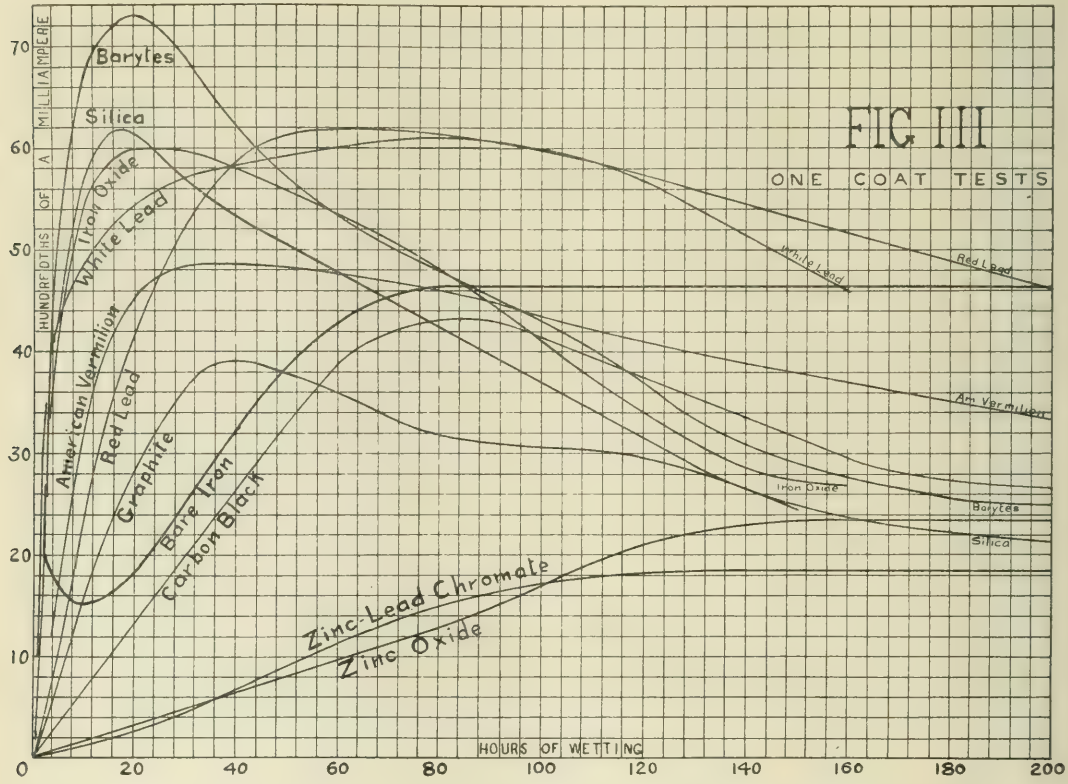
The form of the curves of the one-coat paint tests shows that in several instances, marked depolarizing power is acquired soon after the films begin to disintegrate sufficiently to allow a more rapid absorption of solution and air. Maxima of current values are reached far above that value given by a bare iron cathode when heavily covered with rust. With the two-coat curves the maxima are less pronounced or even do not occur at all.

do increase the rate of depolarization. On Plot I another graphite curve is given which bears out the argument. In this case spirals covered with two very thin coats were used. Up to 50 hours of wetting the excluding power was excellent, but then this decreased very rapidly indeed, and so the rate of depolarization in the film increased accordingly. The maximum is the same as that reached in the one-coat test for graphite on Plot III. Graphite and carbon black are recognized most generally as good excluders, graphite because of the unctuous nature of the pigment. The danger in their practical use lies in getting coats too thin.

Barytes and silica paints are not good excluders,

and these pigments are always used as fillers in other paint mixtures. These paint films possessed the poorest excluding powers and the highest depolarizing powers in the one-coat tests, and next to the poorest and highest in the two-coat tests.

Iron oxide from one- and two-coat tests appears to be not only a poor excluder but a strong depolarizer. The three-coat curve inserted on Plot IV confirms this, representing less protective value than that afforded by two coats of American vermilion. It is also noticeable that the three-coat curve for red lead, though lying decidedly below the two-coat curve, still lies above the two-coat curves for zinc oxide, zinc-lead chromate, and graphite. Unfortunately the white lead curves (and to some extent the red lead and graphite showed up the poorest. It is also interesting to note the relation between the classification of the paint films according to this test, and the classification of the pigments contained in the film according to the Thompson test. As a result of the latter test, Cushman has determined upon calling pigments either stimulators of corrosion, inhibitors or inert (indeterminate) substances. Preserving the order of his listing, a few pigments have been selected from his table, as follows: Inhibitors: zinc-lead chromate, zinc oxide, white lead; Indeterminates: red lead, Princess metallic brown, American vermilion; Stimulators: bright red oxide, carbon black, barytes, graphite. Again excepting carbon and graphite, there is general agreement between

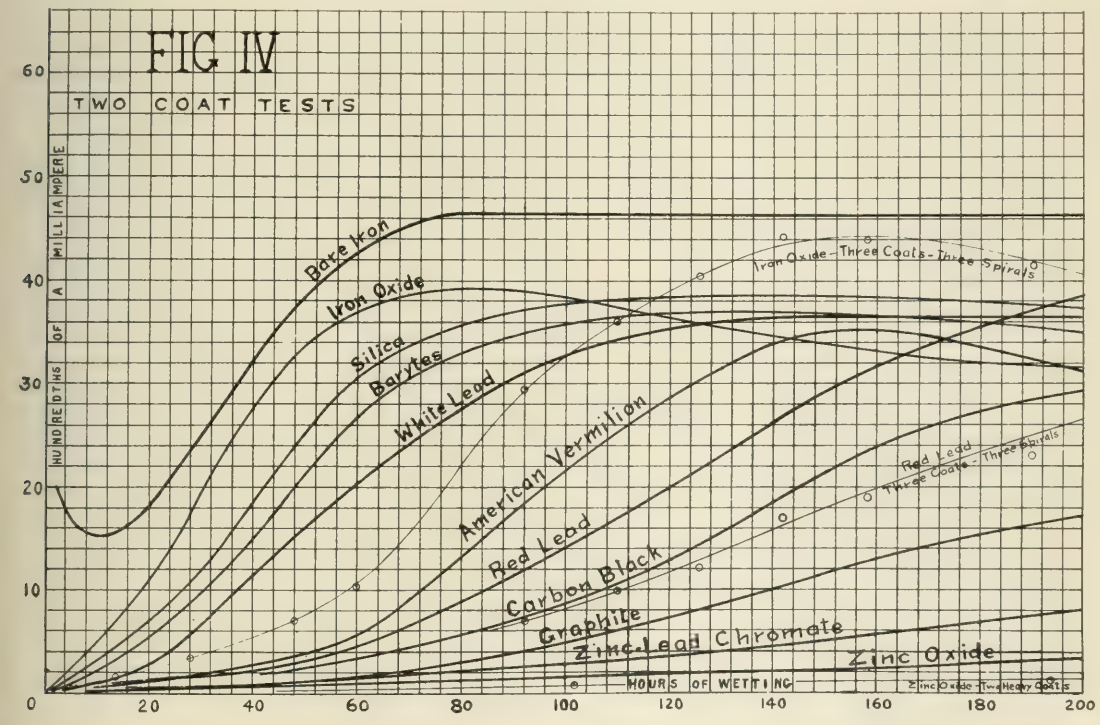


curves) are not determined as accurately as the others. It appears, however, that red lead has better excluding power than white lead, but both films exert equally high depolarizing power. Both red lead and American vermilion give fair excluding power. The lowest curve of Plot IV for zinc oxide represents two-coat tests wherein the films were thick enough to equal very closely the thickness of those films of the three-coat tests of iron oxide and of red lead. The differences in excluding and in depolarizing power is marked.

The first experimental results obtained by Walker and Lewis agree with those obtained now, generally considered, for they used films much thinner than those tested here. That is why in their tests carbon the order of the preceding pigments, and the order of the positions of the current-time curves of the paints made from some of these pigments, and tested by the new method.

At the conclusion of tests the disintegrated paint films were often removed to permit the examination of the iron wire beneath. The wire beneath the zinc-lead chromate film was found to be always bright, and without any etching which would result from local action on the electrode. On the other hand, the wire beneath such films as those of barytes, silica or iron oxide was noticeably etched in numerous places. This is in accordance with the view held regarding the inhibitive power of chromates.

The question naturally arises: What causes the current to fall away so rapidly from the highest maxima? This is hard to answer. All curves reach values lying between 0.15 and 0.25 milliampere at 300 hours of wetting, which is far below 0.466—the value for the well rusted bare iron cathode. From the appearance of the spirals at this time it seems very probable that the pores of the films have become choked up with rust. In fact, some of the coats would not be recognized as paint films. Maxima often occur—especially in one-coat tests before the films show decided failure. That disintegration is in progress is evident, however, from the accumulation of very small blisters all over the film surface. At the maxima, the resistance of the film to passage of electricity or oxygen is at a minimum. It may be that, though the resistance to the passage of the current does not decrease very rapidly, the resistance to the diffusion of air does decrease sufficiently rapidly to cause the rate of depolarization to decrease very fast, especially after the most pronounced maxima. The choking of the pores of the film by even a small amount of rust would account for this.



THE EVALUATION OF PROTECTIVE VALUES.

It would seem most natural to refer all curves to the bare iron curve, calling some value along the curve the value for zero protection. But the curve covers such a range of current values that it is difficult to select any but perfectly arbitrary points. It does not seem justifiable to select 0.466 mg. for the value, as, when this is reached, considerably more rust has accumulated than ever appears on completely disintegrated paint films; nor can a value as low as 0.20 mg. be chosen, as this would greatly undervalue the protection given by all films. Inasmuch as such a method would demand, not only the selection of a perfectly arbitrary point, but a selection that might prove misleading, another method has been adopted.

The curves are current-time curves, and hence the area included between any curve and the co-ordinates corresponding to any point on the curve represents a quantity of electricity. The magnitude of the included area or of the quantity of electricity—in coulombs, for example—is directly proportional to the amount of depolarization that has proceeded up to the same time. The point of time to which to integrate along any curve has been determined in several ways, and thus far no one way has been adopted in preference to the others. The different methods lead to essentially the same results. Thus all areas up to (A) 70 hours or (B) 100 hours of wetting might be integrated; or (C) integrate to the points where the curves pass through some ordinate, as at 0.20 milliampere. Again, the maxima of the curves might be used as points to which to integrate. In this case, the time at which the maximum occurs must be considered. Let it be assumed that the sooner the maximum occurs the more rapid the deterioration of the films; and the greater the magnitude of the maximum, the greater the depolarizing power of the film which, in turn, depends directly upon decrease in excluding power or increase in deterioration. In other words deterioration may

be represented as directly proportional to the area integrated and inversely proportional to the time or to some power of the time. Protective power may be represented as the inverse of this. Hence, $P = C/t^n$, $A = K\,t^n/Q$, where K is a proportionality constant, t the time up to the maximum current, Q coulombs passed through the circuit up to the time t, and n an arbitrarily chosen constant. Relative values have been obtained by calling K unity and by assigning to the exponent n the values (D) 1 and (E) 2. This method may be used only in case of the one-coat tests. The quantitative results of the above methods are, for the sake of brevity, summarized below in a qualitative manner. The capital letters refer to the preceding methods, and the figures to the paint mixtures as follows: (1) zinc oxide, (2) zinc-lead chromate, (3) American vermilion, (4) red lead, (5) white lead, (6) iron oxide, (7) barytes, (8) silica, (9) carbon black, (10) graphite. The higher the position of a number in any column, the greater the excluding power, and as a rule, the less the depolarizing power of the paint film.

Two-coat tests.		One-coat tests.			
A, B.	C.	A.	B	D.	E.
1	—	1	1	2	2
2	—	2	2	1	1
10	10	9	9	10	9
9	9	10	10	9	10
4	4	3	3	3	5
3	3	4	8	4	4
5	5	8	4	8	3
7	7	6	6	6	6
8	8	5	7	5	8
6	6	7	5	7	7

WORK NOT REPORTED.

Although the method uses current values, a large number of electromotive forces were measured, taken after the current readings and after breaking the circuit. Data relative to the change in resistance of the film were thus obtained. Direct measurement of resistance is greatly disturbed by the condenser-like action of the paint films. All this will probably be considered more fully later.

An attempt was also made to determine the cause for certain inexplicable deviations among the average values of the current readings that sometimes occurred during the course of a test. An examination of Plots I and II shows a few widely displaced points, especially on the third curve for red lead. All conditions were guarded as carefully as possible: the electrolyte was kept at constant level, thus preventing change in conductance due to change in concentration. Temperature changes were watched. The resistance of the electrolyte between bare iron cathodes and anodes was only 18.6 ohms, which formed a part of the resistance of the total circuit of about 119 ohms. This being the case and, further, the temperature changes in the tanks being small, no corrections were made in the current readings. These corrections would have accounted for but a few per cent. of the wide deviations referred to above. Except for a few days when the temperature varied $18 \pm 4°$, it varied only $19 \pm 2°$. The change in solubility of oxygen was thus very small, and could not account for the deviations anyway, as they were frequently in the wrong direction.

CONCLUSION.

The work done thus far indicates that the method is sound in principle, reasonably practicable, and reliable, in that under the same conditions of testing, results can be duplicated. It determines definitely, and under artificial conditions made as nearly natural as possible, the excluding power of any paint film against water and air. As regards the testing of paints for use on iron and steel, the method should develop into one of especial value, as the nature of the corrosion through the painted surfaces (according to the electrolytic theory of corrosion) is entirely analogous to the mechanism of the reactions in the paint cell.

It has further been shown that, at least under the conditions maintained in the test—and it is probably true to varying degrees under conditions of actual service—films prepared from certain of the pigments experimented with possess a marked depolarizing action. This may be in part the saturation of unsaturated bonds in the linoxyn by addition of nascent hydrogen, as it has been shown that linoxyn will depolarize hydrogen under the conditions maintained; and it may be due in part to depolarizing properties possessed by the pigments themselves; but it appears that the rate of depolarization is determined largely by the character of the whole film—that is, pigment and vehicle combined. Increasing the porosity or the thinness of a film makes it possible for the depolarizing action to appear, but it apparently does not necessarily cause it to appear. The exact nature of the depolarizing action, and its true relation to the thickness of the film will be investigated more fully in the future.

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A SHORT METHOD FOR THE DETERMINATION OF SOLUBLE ARSENIC IN COMMERCIAL LEAD ARSENATES.

By B. E. CURRY AND T. O. SMITH.

Received October 23, 1911.

As the result of a request for an immediate report on the amount of soluble free arsenic oxid in a sample of commercial lead arsenate, the writers began a series of experiments to develop a method of analysis which would give satisfactory results without incurring the tedious shaking of two liter bottles, eight times daily for ten days as in the procedure outlined in the standard A. O. A. C. method for this determination.

Since it was desired mainly to reduce the time,

the method which naturally suggested itself was one of determining the amount of continuous stirring at room temperature, that would be equivalent to the eighty shakings at intervals during ten days. Accordingly the samples were placed in a thermostat at 20° C. and stirred continuously by means of a hot air engine.

In order that the results might be directly comparable with the results obtained by the A. O. A. C. method it was necessary to use two liter bottles or less than two gram samples of lead arsenate. The thermostat available would not conveniently carry bottles with a capacity of more than 500 cc. and it did not seem advisable to use less than two gram samples.

A few preliminary determinations demonstrated that more than eighteen hours of continuous stirring did not appreciably increase the amount of arsenic oxid in solution. Also these results showed that no obvious direct relation existed between the A. O. A. C. results, and those obtained by continually stirring two gram samples in the thermostat with 500 cc. of water. The solubility of the lead arsenate itself entered in and caused the difference between results obtained by the two methods. The difference in the volumes of water used in the two methods amounted to 1500 cc. This quantity of water dissolves a considerable amount of lead arsenate.

This consideration involved a side problem. It has been pointed out by others, that arsenate of lead may mean the triplumbic arsenate $Pb_3(AsO_4)_2$ or plumbic hydrogen arsenate $PbHAsO_4$. Most commercial samples may consist of a mixture of these two, the amount of each depending upon the method and the conditions under which the precipitation was made. It is evident, also, that in some cases the by-products formed in the process of manufacture have not been washed out. In some samples the odor of acetic acid, which is formed when lead arsenate is made from lead acetate and di-sodium arsenate, would indicate that this step in the manufacture had probably gone no farther than the filter press.

Based on the theoretical percentage of As_2O_5 in lead arsenates consisting of mixtures of $Pb_3(AsO_4)_2$ and $PbHAsO_4$ and also upon the analysis of a number of samples from some of the leading manufacturers, it is evident that most commercial grades carry from 25 per cent. to 33 per cent. of As_2O_5 in the moisture-free product. As the solubility of these lead arsenates is low the variation within these limits is slight and a solubility factor may be determined which introduces no appreciable error within this range.

Lead arsenate is generally put on the market in air-tight containers in order to keep it in a moist condition until ready for use. After it has once been dried it is much more difficult to keep in suspension. This fact suggested the relative rate of solubilities of the dry arsenate and the commercial form which usually contains about 40 per cent. to 60 per cent. moisture. Investigation showed that the moist sample reached its maximum solubility in about 18 hours, while the dry sample required several days. Because of this difference in the rate of solubility it is better to determine the water and then weigh out an amount of the moist sample equivalent to two grams of dry lead arsenate. All the following determinations were made on moist samples. To overcome the inconvenience of washing the moist sample from a weighing tube or watch glass, a small piece of oiled-paper may be balanced on the pan. The sample is weighed on this paper and the paper then transferred to the jar. It is necessary to stir the sample well into suspension with a glass rod before placing the jar in the thermostat.

Several experiments were made to determine the time required to bring the lead arsenate and water into equilibrium. It was found that with the temperature at 20° C. the maximum time was for all practical purposes not more than 18 hours. Satisfactory results were had where stirring had been continued only twelve hours. This makes it easily possible to complete the determination the second day. By the A. O. A. C. method the report is delayed until the eleventh day.

When 500 cc. jars are used as in these experiments, a 200 cc. portion of the solution is a satisfactory amount for analysis. Most lead arsenate solutions do not subside rapidly. In order to obtain a solution free from solid lead arsenate it is usually necessary to pour the contents of the jar on a filter and take the sample for analysis from the filtrate. In a few samples of commercial lead arsenate, small amounts of arsenious oxid were found. The exact amount may readily be determined by simply adding to this 200 cc. portion, the starch and bi-carbonate and titrating with a standard iodine solution.

$$As_2O_3 + 4I + 2H_2O = As_2O_5 + 4III.$$

The addition of bi-carbonate, starch and iodine solution does not interfere with the subsequent determination of arsenic oxide. In the reduction the bicarbonate is neutralized, the starch is converted into sugar and in the acid solution the iodine becomes a reducing agent. Since arsenious oxid is not always present, it is desirable to test for it qualitatively in a part of the solution remaining after the two samples of 200 cc. each have been taken.

The reduction of the arsenic oxide to arsenious oxide in the 200 cc. sample is readily accomplished by the modified method of Mohr. In this laboratory, 5 cc. of sulphuric acid and one gram of potassium iodide are added to the sample in a 400 cc. beaker and the solution boiled until the volume is reduced to 40 or 50 cc. The solution is then cooled and diluted to about 150 cc. In most cases the iodine will not all have been removed and the solution will retain a yellow color. This excess of iodine is removed by the addition of twentieth normal sodium thiosulphate solution added carefully from a burette.

$$2I + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI.$$

If the flask or beaker is of colorless glass and set on a white plate carefully screened from reflected

colors, it is not necessary to add starch to determine the end point. The addition of the starch here is undesirable as will be noted later, and under these conditions the disappearance of the yellow due to the presence of iodine gives a satisfactory end point.

After the excess of iodine is removed the clear solution is made slightly alkaline. A sodium hydroxid solution is more convenient and rapid for this purpose than sodium carbonate and gives satisfactory results. The solution is again made acid with a few drops of dilute sulphuric acid and stirred well to make certain that all alkali is neutralized; the solution is made alkaline again with sodium bicarbonate and is ready for titration. A considerable excess of bicarbonate, as is sometimes recommended, has not been found necessary in these experiments. The solution is titrated with a standard iodine solution according to the equation given for the oxidation of free arsenious oxid in the original solution. Various comments have been made on the use of starch as an indicator in this reaction and many methods proposed for eliminating its objectionable features. A number of these methods were tried in these experiments. The digestion of the starch in dilute hydrochloric acid for twenty-four hours and subsequent drying at 100° C. for three hours is not entirely without merit, but was not found necessary when a good starch was procured and well boiled. The addition of three drops of a ten per cent. solution of potassium iodide increases the delicacy of the end point when only a part of a cubic centimeter of iodine solution is used. When a larger amount is used the potassium iodide in the iodine solution itself serves the purpose and makes further addition unnecessary.

In a few samples the lead was removed as sulphate before beginning the analysis for arsenic; but, with the amount of lead present in these samples, its presence was not found objectionable. The number of cases in which this was investigated, however, and the small amounts of lead present in all the samples preclude any generalization as to how far this statement will hold true.

The results thus obtained include all arsenic oxid in solution and are lower than those obtained by the A. O. A. C. method. This is because the solubility of lead arsenate is left out of consideration and the volumes of water are unequal. In order to fix the relation between the results obtained by the two methods it was necessary first to determine the solubility of lead arsenate. Accordingly, a number of samples were prepared in the laboratory and a number of commercial samples were selected and washed as free as possible from by-products with distilled water. The solubility of the lead arsenate in these samples was determined by stirring at 20° in the thermostat and also by the A. O. A. C. method. It was found that the amount of soluble arsenic determined by the A. O. A. C. method was exactly four times as much as that found by the short method, the amounts being directly proportional to the volumes of water used in the different methods. The average of the results obtained by the A. O. A. C. method calculated to percentage was 0.605 per cent. while the average of the results obtained by the short method was 0.151 per cent. These results include the blank for the end point in the titration. The results obtained by both methods agree very closely. In order to obtain the amount of soluble arsenic not in the form of lead arsenate the above percentage should be subtracted from the total amount of soluble arsenic.

Manufacturers supplied us with 17 samples of lead arsenate which carried various amounts of soluble arsenic oxid. These samples were analyzed for soluble arsenic by the short method outlined above and also by the A. O. A. C. method. The results of these determinations are given in Table I. In this table, column 2 gives the results obtained by the short method; column 3 shows the results obtained by the A. O. A. C. method. No corrections are made in these columns for the solubility of lead arsenate. These results give the total percentage of soluble As_2O_5. These samples contained no soluble arsenious oxid. Column 4 shows the results obtained by the short method after subtracting the factor 0.151 per cent. for the solubility of the arsenate of lead. Column 5 shows the results by the A. O. A. C. method after making the correction of 0.605 per cent. The results given in columns 4 and 5 are practically identical.

TABLE I.

Lab. no. of sample.	Per cent. of soluble arsenic by short method.	Per cent. soluble arsenic by A. O. A. C. method.	Per cent. soluble arsenic. Short method corrected for solubility of lead arsenate.	Per cent. soluble arsenic. A. O. A. C. method corrected for solubility of lead arsenate.
1	0.26	0.70	0.11	0.10
2	0.37	0.81	0.22	0.21
3	0.37	0.85	0.22	0.25
4	0.44	0.83	0.29	0.23
5	0.40	0.85	0.25	0.25
6	0.40	0.91	0.25	0.31
7	0.41	0.92	0.26	0.32
8	0.44	0.92	0.29	0.32
9	0.46	0.96	0.31	0.36
10	0.66	1.12	0.35	0.52
11	0.77	1.26	0.62	0.66
12	0.96	1.50	0.81	0.90
13	1.22	1.79	1.07	1.19
14	1.42	1.98	1.27	1.38
15	1.99	2.50	1.84	1.90
16	2.61	3.03	2.46	2.43
17	3.24	3.78	3.09	3.18

Referring still to the table it is at once obvious that by correcting for the solubility of lead arsenate that the results determined by either method may be quickly changed to terms of the other. The corrected results obtained by the short method give only the soluble arsenic oxid uncombined with lead oxid. On this account it more truly tells the nature and quality of any commercial lead arsenate.

The A. O. A. C. method gives results uniformly 0.605 per cent. higher than the corrected results given by the shorter method. Stated otherwise, when 0.605 per cent. is added to the results obtained by this method the results become the same as those obtained by the A. O. A. C. method and with the expense of much less time. The result of this method

as given in column 4 gives the soluble arsenic oxid not combined with lead oxid.

The method outlined in this paper gives a rapid and accurate procedure for determining soluble arsenic oxid in commercial lead arsenate. It is pointed out that the solubility of lead arsenate affects the total amount of soluble arsenic oxid and a correction is worked out which gives the amount of soluble arsenic oxid not combined with lead oxid.

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VALUATION OF FLUORSPAR.

By E. BIDTEL.

Received January 2, 1912.

In the commercial analysis of fluorspar the determinations usually required are calcium fluoride, silica and calcium carbonate; in some particular cases lead, iron, zinc and sulfur. We have received several calls for percentage of barium sulfate but the most careful qualitative tests have failed to show the presence of this mineral, as will be shown later, in either what is known as Rosiclare or Fairview fluorspar.

There is no practical method for the separation of fluorine from silica and of determining fluorine direct in its ore, which answers the commercial requirements of a mine laboratory. The usual practice followed by most chemists is to determine the total calcium oxide and to calculate from this the amount of calcium fluoride, after deducting the amount equal to the calcium carbonate present, this latter being determined from a separate sample in the usual way by absorbing the liberated carbonic acid in soda-lime tubes. This method would be correct if all the calcium present were combined with either carbonic acid or fluorine and all the carbonic acid present combined with calcium. The first assumption is probably correct as all our experiments go to prove this, but the latter we know is wrong, for lead carbonate, zinc carbonate and iron carbonate are frequently present, especially in the gravel fluorspar. Consequently, the calculated amount for calcium carbonate will be too high and the calcium fluoride in consequence will be too low.

In view of the above error, I have found it better to dissolve all carbonates from the sample by acetic acid, leaving the calcium fluoride and silica as a residue on the filter ready for the determination of both silica and calcium fluoride. It must be remembered that calcium fluoride is slightly soluble in acetic acid. I have reduced this solubility to a factor which I use in my calculations. Generally the amount of calcium carbonate present is greatly in excess of the other carbonates, so that frequently it will be sufficiently accurate for commercial purposes to report the amount soluble in acetic acid after deducting the amount of calcium fluoride soluble in this acid as calcium carbonate. It is to be remembered that at this point there is opportunity for another small error which, however, is limited, varying with the amount of base metals present; should they be present in considerable quantities the residue must be weighed, after drying at 110° C., to avoid an error caused by their oxidation. Ordinarily, however, this oxidation is so small that it need not be taken into account. In the separation of carbonates and ignition of residue, the loss will also include small amounts of water, volatile and organic matter. The residue left insoluble in acetic acid contains all the silica originally present in the ore. The silica is now determined by volatilizing the same as silicon fluoride. The presence of sulfides of iron, zinc and lead must be considered, and for this reason I have found it best to oxidize the sulfides in the residue by heating with mercuric oxide before evaporating with hydrofluoric acid. In this operation lead sulfide is entirely oxidized to lead sulfate, but the ferruginous zinc sulfide is but slightly acted upon and remains unaffected by hydrofluoric acid, in so far as final results are concerned, as shown by analysis of synthetical samples of known percentages.

In regard to the determination of calcium fluoride, I avoid decomposing the sample and eliminate the calcium fluoride by treating the residue obtained from the silica determination with hydrofluoric acid to transform the iron oxide into iron fluoride and extracting the same together with the lead and zinc by solution of ammonium acetate containing ammonium citrate. The method as used at present follows:

Weigh into a small Erlenmeyer flask one gram of the finely powdered sample, add 10 cc. of ten per cent. acetic acid, cover with a short-stemmed glass funnel and heat on a water bath for one hour, agitating from time to time. Filter through a 7 cm. ashless filter, wash with warm water four times and burn off the filter paper in a weighed platinum crucible at a temperature as low as possible. The loss in weight minus 0.0015 gram (the amount of calcium fluoride soluble in acetic acid under the conditions named) is calcium carbonate.

Add to the residue in the platinum crucible about one gram of yellow mercuric oxide in the form of an emulsion in water; break up any hard lumps that may have formed; evaporate to dryness and heat to a dull red heat; cool and weigh. Add about 2 cc. of hydrofluoric acid and evaporate to dryness, repeating this operation twice, using 1 cc. of hydrofluoric acid in each of the last two operations. Add a few drops of hydrofluoric acid and some macerated filter paper, as recommended by Dittrich, then a few drops of ammonium hydroxide to precipitate the iron and evaporate to dryness. Heat to a dull red heat, cool and weigh; the loss in weight is reported as silica. Now add 2 cc. of hydrofluoric acid and a few drops of nitric acid, cover the crucible with its lid and place on a moderately warm water bath thirty minutes; remove the lid and evaporate to dryness. If the contents of the crucible are not now perfectly white, evaporate again with hydrofluoric acid, add a few drops of hydrofluoric acid and 10 cc. of the solution of ammonium acetate (this ammonium acetate is

prepared as follows: neutralize very carefully 400 cc. of eighty per cent. acetic acid in a liter flask with strong ammonium hydrate; add twenty grams of citric acid and fill up to the mark with strong ammonium hydrate). Digest on a boiling water bath for thirty minutes; filter and wash by decantation with hot water containing a small amount of the ammonium acetate solution just described, then with pure, hot water; ignite in the same crucible and weigh. The residue should be perfectly white and should be pure calcium fluoride. To test this, add 2 cc. of sulfuric acid, heat to decompose the calcium fluoride, and evaporate the excess of sulfuric acid; repeat this operation, using 1 cc. of sulfuric acid. Now weigh the calcium sulfate, add five or six grams sodium carbonate, fuse and dissolve in hydrochloric acid in slight excess; should a white precipitate occur at this point it will indicate the presence of barium.

To prove this method I selected clear crystals of fluorspar, pulverized the same and purified it by treating with acetic acid, hydrofluoric acid and ammonium acetate; the washed, dried and ignited powder was decomposed by sulfuric acid and the calcium sulfate weighed. By taking an average of six determinations 0.3875 gram of this fluorspar formed 0.67555 gram of calcium sulfate equal to 99.97 per cent. calcium fluoride. One gram of this fluorspar treated as described showed the following results as an average of twelve determinations:

	Gram.
Loss in weight by treating with acetic acid	0.0015
Loss in weight by treating with HgO and HF	0.0002
Loss in weight by treating with ammonium acetate	0.0012

The amount of calcium fluoride lost in these different manipulations was 0.0029 gram, or 0.29 per cent., if we take one gram for analysis. I now analyzed mixtures of material of known percentage similar in composition to fluorspar and obtained the following results, using one gram for analysis:

	CaF_2.	SiO_2.	$CaCO_3$.	PbS.	ZnFeS.
Taken	85.11	6.66	5.59	1.50	1.14
Found	85.07	6.61	5.57		
Taken	80.05	7.71	7.92	2.50	1.82
Found	80.03	7.70	7.87		
Taken	78.45	8.32	10.40	1.40	1.43
Found	78.41	8.29	10.34		

Average samples of different car loads showed the following percentage, one gram of material being taken for analysis:

		Weighed as CaF_2.	$CaSO_4$ obtained by decomposition with H_2SO_4.	CaF_2 equal to $CaSO_4$.	Average plus 0.29 per cent.	SiO_2.	Average.	Soluble in acetic acid less 0.15 per cent.	Average.	CO_2.	$CaCO_3$ equal to CO_2.
1	Keystone ground.	99.07	172.75	99.06	99.31	0.44	0.45	0.20	0.24	0.116	0.26
		99.01	172.65	99.01		0.49		0.26			
		99.06	172.63	98.99		0.42		0.27			
2	A-1 Ground	96.81	168.80	96.80	97.09	1.47	1.45	0.88	0.88	0.35	0.80
		96.77	168.73	96.76		1.42		0.90			
		96.86	168.89	96.85		1.45		0.86			
3	Gravel	89.49	155.72	89.30	89.58	3.31	3.31	4.27	4.23	1.75	3.98
		89.35	155.69	89.28		3.33		4.17			
		89.38	155.71	89.29		3.29		4.25			
4	Gravel	86.76	151.00	86.59	86.97	4.90	4.93	4.72	4.68	1.95	4.43
		86.87	151.24	86.72		4.93		4.69			
		86.85	151.27	86.75		4.95		4.63			
5	Gravel	82.14	143.03	82.03	82.32	8.59	8.67	6.09	6.13	2.61	5.98
		82.13	143.00	82.00		8.70		6.18			
		82.08	143.10	82.06		8.71		6.12			
6	Unwashed sand	66.02	114.80	65.83	66.14	13.76	13.77	15.52	15.58	6.83	15.52
		66.13	114.86	65.87		13.75		15.57			
		66.04	114.82	65.84		13.80		15.65			

The calcium sulfate obtained by decomposition of fluorspar was fused with sodium carbonate and the cake dissolved in hydrochloric acid. The solution was perfectly clear, showing a total decomposition of the fluorspar and the absence of barium.

As our fluorspar does not contain any gypsum and heavy spar, I did not investigate its influence on the calcium fluoride determination, but it is evident that small amounts of calcium sulfate will be leached out, if present, together with the carbonates. Barium sulfate is easy to detect and can be determined as usual.

The only constituent of injurious influence would be any silicate containing calcium. F. Julius Fohs, in Bulletin 9 of the Kentucky Geological Survey, states the following silicates occurring associated with Kentucky fluorspar: Apophyllite, Datolite, Desmine, Epidote, Laumontite and Natrolite. Apophyllite and Natrolite cannot be present in the fluorspar because there are no alkalies to detect. The same with Datolite. I could not find any trace of boron; Desmine and Laumontite cannot be present in any considerable amount, there being only very small amounts of aluminum in the spar.

I have made a support of aluminum which enables me to handle six crucibles at a time and I can finish six analyses in ten hours.

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DETERMINATION OF MANGANESE IN STEEL.

By JAMES J. BOYLE.

Received December 15, 1911.

After successively trying for some time the color method, Johnson's lead peroxide-sodium arsenite titration method and the ammonium persulphate-sodium arsenite titration method for manganese in steel with varying success, the writer has adopted a suggested

modification of the latter method which gives better and more concordant results, closely approaching the bismuthate method in accuracy.

Experience has shown that the color method cannot be used with all kinds of steel, as various shades of color are obtained, which do not compare well.

Johnson's method gives fairly good results. The chief objection is that some solution upon decanting is always left in the test tube, the error increasing as the manganese in the steel varies from the manganese content of the steel used in standardizing the sodium arsenite solution.

Furthermore, various shipments of lead peroxide did not have the same oxidizing power.

Using Walter's persulphate method, and titrating the permanganic acid obtained with sodium arsenite, gives gratifying results, providing the permanganic acid is kept ice-cold.

In first trying this method in warm weather, difficulty was experienced by the solution rapidly re-oxidizing, so that unless the arsenite was run in rapidly, the results obtained were poor.

It was found that if the solution was warmed a few minutes after the titration was made, re-oxidation would be so complete that if again titrated as before, a practical check could be obtained.

By keeping the solution ice-cold, there is no oxidation and good results are obtained, providing the operator is familiar with the end point, which is a suggestion of yellow, free from pink tints.

A modification of this method was worked out, which produced better results. Briefly, the method is:

Weigh out one gram of steel, dissolve with 100 cc. of nitric acid (sp. gr. 1.20) in a 200 cc. beaker by placing on a hot plate and heating till no more brown fumes appear. Remove from the hot plate, cool and dilute to 500 cc., mixing thoroughly.

Take 100 cc. of the well-mixed solution, corresponding to 0.2 gram of steel, place in a 300 cc. Erlenmeyer flask, and heat on the water bath till warm.

Add 15 cc. of silver nitrate (1.33 grams per liter) and about a gram and a half of ammonium persulphate, warming about a minute or two after the color commences to develop; cool, add a slight excess of sodium chloride (6 cc. of solution containing 1.4 grams per liter) so as to precipitate all the silver; titrate with a standard solution of sodium arsenite till all pink shades are gone, and the white of the precipitated silver chloride alone remains.

This end point is very sharp and more easily determined than that of the other methods. The silver nitrate being all precipitated, no re-oxidation of the reduced permanganic acid can occur.

The sodium arsenite was standardized against a Basic Open-Hearth steel of the Bureau of Standards, sample No. 13-*a*, the results obtained by the various analysts on this steel being more concordant than on the other standard samples.

The accuracy of this method was noted by determining the manganese in four Bureau of Standards samples of steel, the results obtained being within one per cent. of the general averages for these steels.

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CARBON DIOXIDE: ITS VOLUMETRIC DETERMINATION.

By LEON T. BOWSER.

Some time ago there appeared the description of a procedure devised by J. C. Mims[1] for the volumetric determination of carbon dioxide, and from it the writer has succeeded in evolving an accurate and reliable method. There are no new reactions involved, merely an adaptation of well-known principles to a suitable form of apparatus. Stripped of details, the procedure is essentially that of releasing carbon dioxide by means of hydrochloric acid, absorbing it in a strong alkaline solution and measuring the absorbed gas by titration with a standard acid.

Absorption is accomplished in a tower especially designed to meet the conditions. No preliminary guard tubes are necessary, and instead of rigidly excluding water from contact with the potash solution it is the practice to distil over a small amount, thus insuring the mechanical carrying over of residual carbon dioxide along with the water vapors.

The solution previous to titration contains a mixture of potassium hydroxide and carbonate, since bicarbonates do not exist in the presence of alkaline hydroxides. In titrating with an acid, using phenolphthalein as indicator, disappearance of the pink color marks the point at which all hydroxide has been neutralized and the normal carbonate has been converted to bicarbonate or, in other words, the normal carbonate has been half neutralized.

The titration being continued, after adding a drop of methyl orange, appearance of the usual acid reaction denotes complete neutralization of the bicarbonate.

The volume of acid used in the latter titration, then, is just one-half of that required to release all the carbon dioxide from the condition of a normal carbonate. It follows that 1 cc. of normal acid used in the titration between the two end points is equivalent to 0.044 gram CO_2.

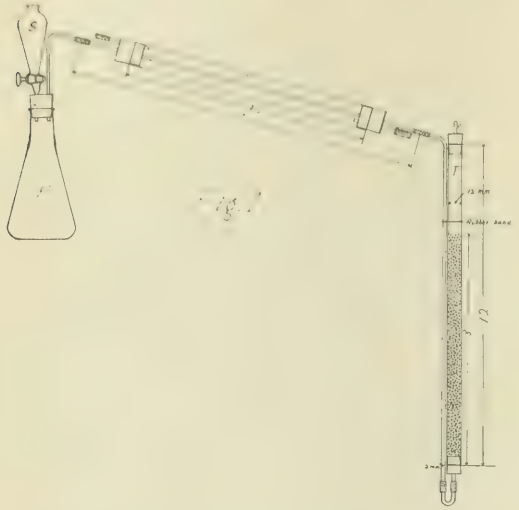
The form of apparatus used is shown in Fig. 1. F is a flask in which the carbonate is decomposed by an acid, which is introduced through a small separatory funnel, S. That used by the writer was originally part of a Geissler alkalimeter, but doubtless could be supplied alone by dealers in apparatus.

In Fig. 2 is shown an easily made substitute; the entire arrangement should be as small as possible, the capacity of the funnel body being about 10 cc. The necessity for the constriction at the top will be explained presently. The condenser C, of Fig. 1, is specially constructed so that the inner tube may be quite short and of as small a bore as possible. All tubing used in the apparatus, except the body of the tower, is of 2 mm. internal diameter, which allows

[1] *Bull.* **65**, 156. U. S. Bureau of Chemistry.

very little space for carbon dioxide to collect and possibly escape absorption.

In the absorption tower T, there are two principal requirements to be fulfilled: securing complete absorption of carbon dioxide, and making the construction such that the carbonated solution may be readily and completely washed out, which bars the use of



any form of potash bulb such as employed for gravimetric work. It is believed that the form of tower shown meets both requirements fully. Merely passing carbon dioxide through an unbroken column of an alkaline hydroxide fails to give complete absorption; it is necessary that the bubbles be completely broken up by means of glass beads or the like.

A suitable amount of sample, usually 1 gram, is now introduced into a 100 cc. Erlenmeyer flask, then about 50 cc. of water are added. The apparatus is connected up, 10 cc. of absorbing solution (50 grams KOH in 100 cc. solution) pipetted into the tower, and sufficient hydrochloric acid introduced through S to decompose all the carbonates in the flask. A word of caution as to the procedure in introducing this acid may not be amiss. First closing the stopcock, the acid is poured into the body of the funnel, then a piece of rubber tubing fitted over the upper end, constricted for this purpose. The admission of acid to the interior of the flask at once releases carbon dioxide and produces sufficient pressure to force out the air, which finds it easier to escape through the funnel than through the absorbing tower, and this pressure must be overcome by blowing through the rubber tube. With very effervescent carbonates the acid is introduced a few drops at a time; with others the entire amount is added at once. After active effervescence has ceased the flask is gently heated, taking care not to force bubbles through the tower too fast, and

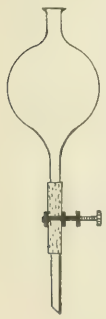


Fig. 2.

water is allowed to distil over until the tower is nearly filled.

The carbonated solution is now transferred to a 100 cc. volumetric flask as follows: The bent end of the inlet tube *a* is placed in the neck of the flask and the solution forced out by blowing through the small outlet tube *b* set in the rubber stopper. This stopper is then removed, the tower filled with water and the latter blown into the flask. Two more washings suffice to rinse out the last traces of alkaline solution, when the contents of the flask are made up to volume. While practical experience has not revealed any trouble from contamination by the carbon dioxide of the breath, yet all possibility of danger may be obviated, if desired, by interposing a soda-lime guard tube properly connected.

To an aliquot of 25 cc. in a 250 cc. beaker or other open vessel is added a few drops of phenolphthalein, followed by 10–15 cc. of 95 per cent. alcohol; then acid of approximately normal strength is run in until the color begins to dim, after which decinormal acid is used to complete the discharge of the pink color. The burette reading is recorded, a drop of methyl orange added, the titration continued to the usual end point, and a second reading made. After subtracting the equivalent of carbon dioxide in the reagents ascertained by a separate blank determination, the difference between the two readings, multiplied by the factor 0.0044 for strictly decinormal acid, gives the grams of carbon dioxide in the aliquot, from which the percentage in the original sample may be easily found.

It is probable that the titration will be found the principal difficulty in the use of the method. Ordinarily the phenolphthalein end point is supposed to give no trouble of any kind, but it is very apt to do so nevertheless. The writer has discovered that the addition of a small amount of ethyl alcohol after introducing phenolphthalein entirely eliminates the difficulties from this source, but without such a precaution it is improbable that a satisfactory end point can be secured. A fuller explanation of this difficulty and the simple remedy for it will be given in a later paper. During this part of the titration the solution should be kept rotating vigorously, since any local excess of acid would carry the reaction on to the point of releasing carbon dioxide from the bicarbonates in the immediate vicinity.

In the addition of methyl orange not more than one drop should be added to 25 cc. of the carbonated solution. When this amount is used the change of color is quite easily noted, but the presence of larger quantities renders observation of the color change a matter of difficulty. The end point to observe is when the clear lemon-yellow of the alkaline solution becomes a shade darker from the admixture of pink of the beginning acid reaction. Dark days or poor light render the observation difficult. When the acid used for the titration is as strong as decinormal the color change is noticeable to the unaided eye, but for acids more dilute it is advisable to have at hand a comparison solution of the same tint as the titrated

olution when alkaline, and the slightest difference of color is then easily noted. Even with the aid of his device a considerable amount of care must be exercised should an acid as dilute as centinormal be in use, but with care and proper light even then the end point is distinguishable with accuracy.

After the development of the method a large number of determinations was made, nearly every one of which was very satisfactory. In the table is presented a summary showing the general run of results. In explanation it may be noted that in some cases two, in others three titrations were made on aliquots from the same flask, given in the column headed "Successive aliquots," while the average of these titration results is to be found under "On det." The last column gives the average of all determinations on each salt.

			Per cent. CO_2 found.		
				Average.	
No.	Salt used.	Per cent. CO_2 taken.	Successive aliquots.	On det.	On salt.
1.....	Na_2CO_3	41.19	41.10		
2.....			41.27	41.18	
3.....			41.10		
4.....			41.27	41.18	41.18
5.....	K_2CO_3	31.27	31.15		
6.....			31.15	31.15	
7.....			31.15		
8.....			31.24	31.19	31.17
9.....	$CaCO_3$	43.96	43.91		
10.....			44.00	43.95	
11.....			44.00		
12.....			44.09		
13.....			43.91	44.00	
14.....			43.83		
15.....			43.91		
16.....			44.00	43.91	43.95
17.....	$BaCO_3$	22.28	22.09		
18.....			22.35		
19.....			22.53	22.32	
20.....			22.53	29.75	
21.....			22.35		
22.....			22.53	22.47	
23.....			22.35		
24.....			22.35		
25.....			22.35	22.35	22.38
26.....	$SrCO_3$	29.81	29.57		
27.....			29.92	29.75	
28.....			29.75		
29.....			29.83	29.79	29.77

Of the salts used the latter three had been freshly opened, and presumably were of nearly the theoretical composition. In the case of sodium and potassium carbonates the bottles had been opened several times previously and it was thought some moisture might have entered. On this account the carbon dioxide content was carefully determined by direct titration with a standard acid, giving the percentages shown under "Per cent. CO_2 taken," both of which are slightly below theoretical. All five salts were J. T. Baker's analyzed products, purchased especially for the purpose. As may be noted the average results are, in all but one case, slightly lower than theoretical, which is as it should be, since slight traces of impurities and moisture are nearly certain to be present. As a whole this series is very satisfactory and shows that the method is not lacking in accuracy. Equally favorable results have been obtained in the case of samples in which the carbon dioxide had been determined both in this way and with the Knorr method.

Sulphuric acid should not be used to release the carbon dioxide from a material. A long study of this point, involving numerous determinations, has shown that it will not uniformly decompose carbonates in this form of apparatus. Hydrochloric acid, on the other hand, gives a very perfect decomposition. Numerous trials have shown that, contrary to what might be expected, the acid is not appreciably carried over during the determination, although even if small amounts did accompany the steam no harm could be done.

Another point studied was as to the relative efficiencies of $Ba(OH)_2$, NaOH and KOH for use in the absorbing tower. It was speedily found that $Ba(OH)_2$ cannot be used since it is not possible to prepare a solution greatly exceeding $N/4$ in strength, which is entirely too weak for the purpose.

Using NaOH or KOH there is no difficulty in preparing a solution of any desired strength, although the best results are attained by the use of rather concentrated solutions. The 10 cc. taken is more than sufficient to absorb one gram of carbon dioxide, which would be equivalent to a two-gram sample of nearly any of the purest carbonates. On the whole sodium hydroxide is the less satisfactory in use, there being too great a variation between the titration results of successive aliquots. Potassium hydroxide has given uniform satisfaction both in manipulation and from the standpoint of accuracy.

Either hydrochloric or sulphuric acid may be used for the titration, either giving good results. For ordinary work the most satisfactory strength is decinormal, which gives a clear, easily noted color change with both indicators. When unusually small amounts of carbon dioxide are to be determined, acids of $N/50$ or $N/100$ strength are employed, the former being used in most cases. Their use is justified only in the most exact work, however, since the increased time and difficulty involved cuts down heavily on the speed of the work.

While this method is on the whole as accurate as any of those now employed, the speed attainable by its use is much greater. With but a single apparatus it is possible to make 24 determinations in an eight-hour day, with abundant time between successive distillations. There are no fragile nor unusual parts necessary in the apparatus, nothing to get out of order, and the entire construction is flexible enough to stand a great deal of rough usage. It is easy to construct in almost any laboratory, and in case of breakage replacement is the work of but a moment.

In conclusion, the writer desires to acknowledge his indebtedness to the following for many helpful suggestions: Profs. F. E. Edwards and C. E. Bradley, both formerly of the Oregon Agricultural College, and J. C. Mims, whose published results afforded a starting point for the evolution of the method.

DAYTON, OHIO.

THE VALUE OF THE HIGHER PHENOLS IN WOOD-PRESERVING OILS.

By Samuel Cabot.

Received September 28, 1911.

Recent investigators claim that the tar acids in creosote oils have little or no value for the preservation of timber. The reasons given are that the ingredients are volatile and somewhat soluble. This supposition is partially confirmed by analysis of preservative oils extracted from timber which have been in the ground for a long time. The extracts appeared to consist of heavy oils boiling above 250° C. and containing but a trace of phenols. The unsatisfactory part of these tests has been that in only a very few cases was the phenol content of the original oil known. In cases where the percentage of phenols was known, they were the lower carbolic and cresilic acids which are soluble and volatile. It does not appear that any investigator has claimed that the phenols are not the best wood preservative ingredients of creosote oil so long as they are contained in the wood. The only claim is that they have but temporary value. While this appears to be true of the lower phenols, the higher-boiling tar acids have a different character. Their fungicidal qualities are greater than the lower ones, their boiling points are very high and they are practically insoluble. The following experiments show that the phenols in high-boiling oils evaporate more slowly than the oil fraction in which they are contained.

Two grams each of heavy creosote oil and of phenols extracted from the same were exposed on a watch glass at a temperature of from 50–55° C. for two hundred hours and the loss of weight noted at stated intervals. The residue of oil left on the watch glass was a viscous fluid. That of the tar acids had a pitch-like consistency at 15° C. The following tables are taken from many giving similar results.

No. 2 Tar Acids.

Temp.	Time. Hours.	Loss. Per cent.
50–55	1	1.35
50–55	4	3.5
50–55	7	7.6
50–55	12	8.8
50–55	15	10.2
50–55	18	10.5
50–55	43	15.6
50–55	67	18.8
50–55	94	20.8
50–55	140	23.0
50–55	164	24.3
50–55	188	25.3
50–55	200	25.75

No. 1 Heavy Creosote Oil.

50–55	1	2.1
50–55	4	6.35
50–55	7	9.5
50–55	12	10.0
50–55	15	11.25
50–55	18	12.1
50–55	43	16.5
50–55	67	22.2
50–55	94	25.5
50–55	140	32.1
50–55	164	34.3
50–55	188	36.6
50–55	200	36.3

The tar acid residue in these experiments when boiled with a 35 per cent. solution of caustic soda was apparently insoluble. It was also insoluble in a 25 per cent. solution. Another portion of the tar acid residue was then dissolved in 90 per cent. of its weight of benzole, extracted with a warm 10 per cent. solution of caustic soda three times. The benzole became a dark translucent color, the caustic soda a clear brown and a black tarry layer remained between, after settling over night. The caustic soda extract was washed free from tarry matter with benzole, neutralized with sulphuric acid and extracted with ether in the usual way. This extract was found to contain less than 10 per cent. of the original tar acids dissolved in the benzole. It was found that the tarry layer was partially soluble in water, while the remainder after washing with water redissolved in benzole, showing that it had been dragged down only mechanically.

From these experiments it appears that the methods now in use for the analysis of creosote oil do not show the actual amount of higher phenols present, especially in oils extracted from wood for ascertaining the most permanent wood preservatives. A common practice is to redistil the oil and then analyze the distillate, disregarding the pitchy residue. The distillation would decompose the higher phenols to a considerable extent and as a greater part of them are non-volatile, they will supposedly be found in the pitchy residue. Again in the second step of the analyses a greater proportion of the tar acids could be dissolved in the caustic soda if a dilute solution were used and very much less in a more concentrated one. Under the most favorable conditions, however, it would be only a small part of the total.

The above experiments go to show that previous investigations referred to have found nothing to prove that the high-boiling phenols are not the most valuable ingredients in wood preservative creosote. On the contrary their gummy consistency gives them great physical advantage over straight oil, they are less volatile than the oil, are practically insoluble, and have fungicidal qualities far greater than any other of the products of creosote.

COMPOSITION OF DRY GLUTEN AND ITS RELATION TO THE PROTEIN CONTENT OF FLOUR.

By Geo. A. Olson.

Received October 30, 1911.

In comparing the dry gluten and protein content of flour, Thatcher[1] found that the gluten content was in close agreement with the protein content of medium and high-protein flours (N × 6.25), and frequently several per cent. lower in low-protein flours. Occasionally flours were found low in protein with a relatively high gluten content and *vice versa*. It occurred to the writer that perhaps the reason for high-protein flours containing relatively higher

[1] Wash. Exp. Sta., *Bull.* **84**, 33.

glutens than did flours low in protein was due to a larger amount of impurities in the former.

It is needless at this time to enter into a complete historical account of the work done by different investigators along the line of gluten research. It might be well, however, to mention the fact that gluten as it is ordinarily prepared, according to Osborne,[1] contains besides "the greater part of the protein matter of seed, starch, fat, lecithin and phytocholesterin, and possibly some carbohydrate substance or substances of as yet unknown character. The chief constituents of the gluten are the two proteids, gliadin and glutenin. Norton[2] states that gliadin and glutenin make up about 75 per cent. of the true gluten of flour, the other constituents being non-gluten, mineral matter, fat, starch, fiber and other non-protein matter. Ritthausen[3] found four proteids in gluten. Fleurent[4] found three proteids, and Osborne and Voorhees[5] found two proteids. Recent work by J. König and P. Rintelen[6] support Ritthausen's views.

In our wheat and flour investigations at this Station it has been found that straight flour from Palouse wheats show variable gluten content, when compared with the protein content (N × 6.25) of the respective flours. With these glutens at command and after a few preliminary experiments had been conducted, it was decided to investigate the reasons for the variations with a view of throwing some light on the baking qualities of the various flours under study. The glutens used for this series of investigations had been prepared by mixing 20 grams of flour and 12 cc. of water, allowing the mixture to stand for one hour, and then washing out the starch with a stream of water. A bolting-cloth was held beneath the kneaded dough in order to prevent the loss of the fine particles of gluten generally carried down with the water. After having removed as much of the starch as can possibly be done mechanically, the resulting wad of gluten was run over the bolting-cloth to pick up the fine particles. It is this gluten, after drying for twenty hours, which shows a variable quantity when compared with the protein of the flour.

The glutens studied were from flours representing wheats of the type of Bluestem, Red Russian, Turkey Red, Fife, Dale, Little Club, Galgalos and some of the Station hybrids. Particular attention was given to selecting flours containing average, high, and low glutens. No marked differences were observed in the comparisons between high-protein flours and their glutens, while on the other hand several flours with at least 10 per cent. protein (N × 6.25) yielded glutens amounting to a little over 7 per cent. dry gluten.

Determinations of moisture, ash, starch and nitrogen were made of the different glutens selected. The nitrogen and ash determinations were made according to the A. O. A. C. methods. Thoroughly dried samples of gluten were ground at a temperature of about 35° C. and finally capped tight in vials of the same temperature. The procedure eliminated moisture absorption to a minimum, while, on the other hand, it may have reduced the actual amount of moisture contained within the gluten. As comparative results were all that were desired, the writer can see no objection to the method, and the water thus found must have been either sealed up when drying the gluten the first time or water of combination.

The starch determinations were made by hydrolyzing the starch according to the writer's method[1] and the results thus obtained were in some cases checked by the Sachsse method.[2] Unlike starchy substances, such as feeding-stuffs, cereals, etc., it is difficult to determine the exact point of complete hydrolysis of gluten, due to the fact that comparatively little of the product enters into solution, thus making it difficult to observe the exact end point. With some judgment, however, little, if any, difficulty was encountered in the method. Repeated hydrolysis at different times gave results fairly concordant with those previously found. When compared with the Sachsse method no appreciable differences were observed. The peculiar reduction of the copper with the hydrolyzed gluten solutions will be discussed in the following paragraph.

Only a few of the copper reductions behaved like ordinary reducing substances when brought in contact with the Fehling solution, while, on the other hand, most of them produced flocculent precipitates on boiling, which were in some cases difficult to filter. The color of the reduced copper varied from a copper-red, light yellow to a dark brown. Those having the familiar copper color, and in every respect similar to sugar reduction of copper, are undoubtedly the hydrolyzed starch. Those having produced flocculent precipitates are no doubt admixed with some protein complex, probably mucoid-like substances or other protein loosely bound. The differences observed in different hydrolyzed glutens were quite marked, and repetitions gave similar characteristics in the same gluten as previously observed.

Repeated digestions of gluten with either calcium or barium hydroxide, filtering and precipitating the resulting filtrate with acetic acid, separating the acetic acid precipitate from liquid, followed by the hydrolysis of both precipitate and liquid with sulfuric acid and then neutralizing with sodium hydroxide, showed no reduction when brought in contact with Fehling's solution. According to this procedure neither a mucin nor mucoid-like substance could be confirmed.

The results of the analyses of the crude glutens representing flours made from different types of wheat have been summarized in Table I.

The data given in Table I clearly show that crude gluten has a variable nitrogen, ash, starch and

[1] Carnegie Inst., Washington, *Pub.* **84**.
[2] *J. Am. Chem. Soc.*, **28**, 8–25 (1906).
[3] *J. prakt. Chem.*, **85**, 213 (1862).
[4] *Compt. rend.*, **1896**, p. 327.
[5] *Am. Chem. J.*, **15**, 392 (1893).
[6] *Z. Untersuch. Nahr.-Genuss.*, **8**, 401–407 (1904).

[1] This Journal, **1**, No. 7 (1909).
[2] *Chem. Centr.*, **1877**, 732; *J. Anal. Chem.*, **2**, 153.

moisture content. The high starch content due to flocculent precipitation of copper should be attributed to other substance or substances than starch, the nature of which are as yet unknown.

TABLE I.—ANALYSES OF CRUDE GLUTEN MADE FROM STRAIGHT FLOURS.

	Per cent. N.	Per cent. ash.	Per cent. calculated as starch.	Per cent. water.
Average 24 samples	12.77	1.84	5.20	2.13
Maximum	14.09	3.08	12.70	3.82
Minimum	11.28	1.34	0.11	0.90

Although the results given in the above table do not show the variations in the amount of dry gluten compared to the protein content of the flour, comparable and extreme variations of gluten to protein of flour were nevertheless taken for this study. It might be of some value, however, before going further to state that abnormally low per cents. of dry gluten compared to protein of flour are not necessarily any richer in nitrogen, more free from ash, etc., than one equal to or higher in per cent. of gluten to protein of flour. The data for the nitrogen and protein of wheat and flour, the nitrogen in the gluten expressed in per cent. of the flour, and the per cent. of wet and dry gluten are summarized in the following table:

TABLE II.—DISTRIBUTION OF NITROGEN IN WHEAT, FLOUR AND GLUTEN AND PER CENT. OF GLUTEN IN FLOUR.

	Per cent. nitrogen in			Per cent. protein in		Per cent. gluten.	
	Wheat.	Flour.	Gluten, in per cent. of flour.	Wheat.	Flour.	Wet.	Dry.
Av. 24 samples	1.89	1.73	1.29	11.81	10.81	30.82	9.88
Maximum	2.52	2.27	1.87	15.75	14.19	46.83	14.75
Minimum	1.33	1.29	0.86	8.31	8.06	19.39	7.20

It will be seen from the data given in the above table that percentagely the amount of nitrogen entering into the gluten make up is considerably less (74.6 per cent. of total nitrogen on an average) than that found in straight flours. The data further tend to show that flours high in protein are also high in gluten and flours of average protein composition or less yield percentagely lesser amounts of dry gluten than do flours of higher protein composition. Whether or not the gluten nitrogen is wholly made up of gliadin and glutenin nitrogen will be discussed at some other time.

It has been known for some time that in the process of washing out the starch from flour to get gluten, that some glutens have the tendency to scatter more than others, and as a result are difficult to gather into wads. Other flours, however, yield glutens with strong adhesive qualities and as a result tend to hold the gluten particles together in the process of washing. These characteristics have been attributed to the proportion of gliadin to glutenin contained in the flour.

Gluten determinations in flours of unusually low gluten content were repeated and it was found that these flours had a tendency to scatter and losses would vary, depending upon the care exercised in washing out the starch from the flour. Undoubtedly some of the particles of gluten pass through the bolting-cloth as was indicated by an examination of the washings and the variable yields obtained in dry gluten. By indirect means it was possible to overcome the tendencies of the glutens to scatter. This was accomplished by mixing equal quantities of flour containing scattering gluten with one devoid of these characteristics. The weight of the wet and dry gluten in the non-spreading gluten flour being known, the weight of the wet and dry gluten in the other flour can be calculated from the results obtained with the mixture. The results obtained are as follows:

TABLE III.—COMPARISONS OF THE AMOUNT OF GLUTEN OBTAINED BY THE DIRECT AND INDIRECT METHODS.

	Direct.		Indirect.		
No.	Per cent. wet gluten.	Per cent. dry gluten.	Per cent. wet gluten.	Per cent. dry gluten.	Per cent. protein in flour.
3	20.78	7.66	26.95	7.66	8.19
5	12.78	4.63	23.17	8.94	8.19
11	22.54	8.88	23.11	8.54	8.19
23	21.51	7.23	21.12	9.49	8.06
24	20.00	6.94	24.64	8.81	8.13
25	12.70	4.44	27.35	9.40	8.19
27	20.69	7.16	20.85	7.76	8.06
28	19.29	6.70	18.79	7.30	8.19
34	25.51	8.82	28.98	9.59	9.88
37	13.30	4.57	18.81	6.40	6.38
38	18.04	6.41	31.28	10.00	8.56
39	12.44	4.40	21.20	7.36	6.56
43	17.89	6.25	21.09	6.85	8.06
47	26.54	9.61	39.78	13.86	12.13
62	24.37	9.40	35.04	11.58	10.31
64	27.69	9.59	33.22	11.68	11.38
68	24.94	9.52	39.36	12.86	10.44
69	30.53	10.97	39.84	12.63	11.88
70	18.93	7.09	26.58	9.60	8.75
72	19.99	7.30	32.20	10.78	8.06
76	21.40	7.95	33.28	11.19	9.88
78	20.72	8.01	35.08	11.38	9.94

In every case where the indirect method was put into use, results comparable with the protein content of the flour were obtained. The reason why the glutens of low-protein flours are several per cent. lower than in flours containing a medium or high-protein content is undoubtedly due to the scattering of the gluten and as a result a part of the gluten is lost, hence lower yields of gluten are recorded than are actually present.

The above method of blending flours, having glutens that tend to scatter, with flours having glutens with strong adhesive characteristics will give much higher yields of gluten, sometimes as much as 100 per cent. more than can be obtained by the direct process.

Those who make it a practice to determine the gluten content of flours and base their opinions on the results for the yield of gluten as obtained by the direct process are apt to obtain erroneous data, since at least 25 per cent. of the flours examined by the writer had glutens which tend to scatter in the process of preparation. It is, therefore, necessary to consider whether or not the glutens scatter and in such cases a blend with a strong flour will overcome the scattering tendencies, as well as give more correct

results than can be obtained by the direct method as it is commonly practiced.

CONCLUSIONS.

1. Gluten as it is ordinarily prepared has a variable nitrogen, ash, starch and moisture content.

2. The peculiar copper reduction resulting from adding the filtered extract from hydrolyzed gluten by acid is undoubtedly due to some other substance than starch or sugar.

3. An average of about 75 per cent. of the total nitrogen of flour enters into the crude gluten.

4. Glutens obtained from low-protein flours are not necessarily any richer in nitrogen, more free from ash, etc., than glutens derived from medium- or high-protein flours.

5. The reason why low-protein flours yield much lower per cents. of gluten than medium- or high-protein flours may be attributed to the scattering of such glutens, resulting in mechanical loss. By blending such flours with strong gluten flours, results in yields comparable to those obtained for medium- and high-protein flours.

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A COMPARATIVE STUDY OF METHODS FOR THE DETERMINATION OF HARD AND TOTAL SOFT RESINS IN THE HOP.

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Received October 17, 1911.

Previous to taking up some chemical investigations at this laboratory it became necessary to devote some time to a study of methods for the determination of hard and total soft resins in the hop. Some very interesting results have been obtained which the authors think may be of value, especially to those connected with the brewing industry where the correct valuation of hops is of considerable moment. The results given may also be of some use to the work recently undertaken by a Committee of the International Barley and Hop Prize Exhibit at Chicago for the establishment of definite hop standards.

Previous investigations have shown that there are at least three so-called resins which are constituents of the hop cone, one "hard," tasteless resin and two "soft" bitter resins. Although a considerable amount of research has been done on the nature of these substances and their function in brewing, much is still obscure and in doubt. It is generally agreed, however, that the hard resin is of little or no commercial value, while investigations indicate that the major part of the real brewing value of hops lies in the soft resins, thus making their estimation of considerable importance.

In this study two different methods for the determination of both hard and total soft resins have been given a test: Briant and Meacham's[1] method and Siller's[2] method. The original volumetric method of Lintner[1] and the modified Lintner[2] method for total soft resins have also been studied. Although the original Lintner method has been shown to be inaccurate we have included it in this study because we have found from our correspondence that this method is still employed in a few instances. A method devised by us is given and the comparative results are reported. We have had good success in the use of this method, and while not claiming originality for the basic principles involved, we believe it overcomes some of the objections to present methods. For convenience it is here designated as "authors' method." Not all of the methods for the estimation of hop resins are given, but we believe all have been included that are receiving any extensive use.

METHODS.

In all the methods which have been devised for the determination of hop resins, the separation of the soft resins from the hard resin is dependent upon the ready solubility of the former in petrolic ether, the latter being practically insoluble in this solvent. The extraction of total resins from the hop is effected with ordinary ether.

Briefly stated, the methods compared are as follows:

Briant and Meacham's[3] *Method.*—About four grams of hops are placed in a Soxhlet extractor and extracted for twenty-four hours with petrolic ether (boiling point 50° C.). After the extraction is completed the extraction flask is disconnected from the apparatus and its contents filtered while hot through a small filter paper into a tared wide-mouthed flask; the filtrate is then gently evaporated. The final drying operation is completed by placing the flask on its side in a hot water oven, where it is maintained at a temperature slightly above the boiling point of the ether until its weight is constant. The extract thus obtained is the total soft resins in the sample.

The hops left in the extractor from the petrolic ether extraction are next extracted with ordinary ether for 12 hours. The ethereal extract is then filtered into a tared flask, dried and weighed as in the previous extraction, the residue obtained being estimated as hard resin.

Siller[3] *Method. Soft Resins.*—A ten-gram sample of hops which have been ground through a small meat grinder is placed in a Soxhlet extractor and extracted with petrolic ether (boiling point 30–40° C.) for 8–10 hours. The petrolic ether extract is then evaporated *in vacuo* on a water bath at 40° C. until all of the solvent is removed. The residue is then taken up with methyl alcohol to separate the wax present, filtered and made to 100 cc. volume. A 10 cc. aliquot (equivalent to 1 gram of hops) is placed in a weighed flask and the alcohol is then completely evaporated in a drying oven at 80°

[1] *J. Fed. Inst. Brewing*, **3**, 233 (1897).
[2] *Ztg. Untersuch. Nahrung-Genuss.*, **18**, 241.
[1] *Ztg. Ges. Brawesen*, **21**, 407.
[2] *Chem. Ztg.*, **32**, 1068; O. Neuman, *Wochenschrift für Brauerei*, **1910**.
[3] *I oc. cit.*

C., the evaporation requiring 4–5 hours. The residue obtained is estimated as total soft resins.

Total Resins.—A ten-gram sample of ground hops is placed in a Soxhlet extractor and extracted 8–10 hours with ordinary ether. The ethereal extract is then evaporated *in vacuo* at 40° C. until all of the ether is removed. The residue obtained is taken up with methyl alcohol to separate the wax, filtered and the filtrate made to 100 cc. volume. A 10 cc. aliquot (equivalent to 1 gram of hops) is placed in a weighed flask, evaporated and weighed in the manner used in the determination of total soft resins, the residue obtained representing the total resins in 1 gram of hops.

The hard resin is estimated by difference between the amounts of total resins and soft resins.

Lintner's[1] *Volumetric Method for Soft Resins.*—This method is based upon the fact that the two bitter substances commonly called soft resins react in solution as monobasic acids with alkalies.

A ten-gram sample of hops is introduced into a 500 cc. flask having also a mark at 505 cc.; 350 cc. of light petrolic ether (boiling point 30–50° C.) are added and the flask attached to a reflux condenser. The flask is then heated on a water bath and the extraction continued for eight hours. When cooled to 17.5° C. the liquid is made up to the 505 cc. mark, well shaken and then filtered. One hundred cc. of the filtrate are mixed with 80 cc. of alcohol, 10 drops of phenolphthalein solution (1:100) added, and then titrated with a tenth-normal solution of potassium hydroxide until the red tint just appears. A blank experiment is made to ascertain the amount of potassium hydroxide neutralized by the mixture of alcohol and petrolic ether. The number of cc. required for the titration multiplied by the factor 0.04 (the molecular weight of the bitter substance taken as 400) represents the amount of soft resins in the aliquot.

Modified Lintner Method[2] *for Soft Resins.*—The determination is carried out in the same manner as in the original Lintner method except that the hops are ground previous to the extraction.

Authors' Method.—Ten grams of hops are placed in a Soxhlet extractor and extracted with ether for 8–10 hours. The ethereal extract thus obtained is filtered and the filtrate made to 200 cc. volume.

Total Resins.—One hundred cc. of the ether solution (equivalent to 5 grams of hops) are placed in a 250 cc. Erlenmeyer flask and nearly all of the ether removed by distillation on a water bath at about 40° C. The last portion of the ether is completely removed by drying in a vacuum desiccator at room temperature. The residue remaining is then taken up with alcohol to free the wax, filtered and the filtrate made to 100 cc. volume. A 20 cc. aliquot (equivalent to 1 gram of hops) is transferred to a tared beaker and the alcohol removed by evaporation in a vacuum oven at 50° C. to constant weight. The residue thus obtained is the total resins in one gram of hops.

Total Soft Resins.—The remaining 100 cc. of the original ether extract are transferred to a 200 cc. Erlenmeyer flask and the ether nearly removed by distillation at low temperature, the last portion being removed by evaporation in a vacuum desiccator at room temperature. The residue is taken up with about 100 cc. of petrolic ether (boiling point 40–45° C.). The residue is worked up in the solvent with a glass rod and then let stand a short time to effect the complete solution of the soft resins in the solvent. The hard resin is then removed by filtration. The petrolic ether is removed from the filtrate in the same manner as the ether in the first part of the determination. The residue is taken up with alcohol to remove wax, filtered and the filtrate made to 100 cc. volume. An aliquot of 20 cc. (equivalent to 1 gram of hops) is transferred to a tared beaker and evaporated and weighed as under the determination of total resins.

The hard resin is estimated by difference between the total resins and soft resins.

EXPERIMENTAL PART.

Five samples of Oregon hops of the 1910 crop were analyzed, using each of the different methods given above. Sample No. 1 was an air-dried sample and Nos. 2–5 were commercial samples which had been kiln-dried. In each instance the extraneous matter, such as leaves and stems, was separated, only the whole unbroken cones being used for the determinations. The results of the analyses are given in Table I.

The table shows a wide variation in the results obtained by the different methods. Siller's gives extremely high results for soft resins while Briant and Meacham's and the original Lintner method show very low results. The amount of soft resins obtained by Lintner's modified method and the authors' method agree fairly well. Briant and Meacham's method shows very high results for hard resins while Siller's and the authors' give much lower amounts.

The low results for soft resins obtained by the Briant method and the original Lintner method are due to the fact that the extraction of the soft resins is not complete. The lupulin granules of the hop cone must be well broken up before the soft bitter resins can be completely extracted with petrolic ether. Siller[1] has already pointed out this fact and has suggested the grinding of the hop previous to the extraction as a means of overcoming this defect. Grinding by means of a meat grinder or with sand in an ordinary mortar has been found satisfactory for the preparation of the samples for extraction. When the meat grinder is used, the sample is taken after the material has been ground.

The high percentage of hard resin secured by Briant and Meacham's method is due to the presence of soft resins left from incomplete extraction with

[1] *Loc. cit.*

[2] *Chem. Ztg.*, **32**, 1068; O. Neuman, *Wochenschrift für Brauerei*, **1910**.

[1] *Loc. cit.*

TABLE I.—THE RESIN CONTENT OF OREGON HOPS BY DIFFERENT METHODS.

Method.	Sample 1. Hard resin. Per cent.	Sample 1. Soft resin. Per cent.	Sample 1. Total resin. Per cent.	Sample 2. Hard resin. Per cent.	Sample 2. Soft resin. Per cent.	Sample 2. Total resin. Per cent.	Sample 3. Hard resin. Per cent.	Sample 3. Soft resin. Per cent.	Sample 3. Total resin. Per cent.	Sample 4. Hard resin. Per cent.	Sample 4. Soft resin Per cent.	Sample 4. Total resin. Per cent.	Sample 5. Hard resin. Per cent.	Sample 5. Soft resin. Per cent.	Sample 5. Total resin. Per cent.
Briant and Meacham's	8.00	9.09	17.09	7.95	9.14	17.09	11.54	8.84	20.38	11.37	8.59	19.96	7.54	8.68	16.22
Siller's	2.89	20.07	22.96	2.76	16.50	19.26	2.52	21.49	24.01	1.93	20.96	22.89	1.33	17.01	18.34
Authors'	1.97	16.78	18.75	1.29	15.79	17.08	1.52	18.50	20.02	1.79	17.29	19.08	1.89	13.73	15.62
Lintner's original		8.88			8.00			5.20			6.80			6.40	
Lintner's modified		16.60			16.00			19.32			18.00			13.20	

petrolic ether. Another slight error in this method is caused by the failure to separate the wax but this is not great, the amount of wax present amounting to only 0.25–0.35 per cent.

The extremely high results for soft resins given by Siller's method has been found to be due to the extraction of material from the ground hop seed. The method was worked out, no doubt, with seedless continental hops and consequently this point did not receive consideration. It has been found in this laboratory that although the unground seed gives no appreciable extract with petrolic ether or ordinary ether, the ground seed yields a considerable amount. Seeds taken from four different samples of Oregon hops were ground and extracted in Soxhlet extractors with ether and petrolic ether. The results obtained are given in Table II.

TABLE II.—EXTRACTIVE MATTER IN GROUND HOP SEEDS.

	Sample. No. 1. Per cent.	Sample. No. 2. Per cent.	Sample No. 3. Per cent.	Sample No. 4. Per cent.
Petrolic ether extract	24.05	24.72	27.30	20.36
Ether extract	26.52	26.04	21.70	29.64

There is approximately 25 per cent. of the ground seed which is soluble in each of these solvents. This would permit a large error in the determination of soft resins in seeded hops, especially in Pacific Coast hops where the amount of seeds is high, ranging from 15–20 per cent.

The estimation of hard resin by taking the difference between the amounts of total and soft resins obtained from separate samples is often inaccurate because of the wide variation in the resin content of the samples. Duplicate 10-gram samples of the same hops sometimes show a variation of $1^1/_2$ per cent. in the amount of total resins where total content is only 17 per cent. A difference of $^1/_2$–$^3/_4$ per cent. is common. This is shown to be due to the wide variation in the resin content of the cones themselves by the following experiment: Six cones of different sizes were selected from each of three different commercial samples, their weight taken, and the amount of total resin in each cone estimated by extracting with ether and drying to constant weight *in vacuo* at 50° C. The results are tabulated in Table III.

The differences between the maximum and minimum percentages of total resin in the cones from each of the samples are 3.87, 3.82 and 6.88 per cent. respectively. The most notable difference is in cones II and III of sample No. 3 where two cones of practically the same weight differ 6.88 per cent. It is evident from these results that samples of at least 10 grams weight must be used for the determination of resins, and where accurate results are desired it has been found advisable to make triplicate determinations. The determination of hard resins, furthermore, should be made on the same sample as used for soft resins.

Lintner's modified volumetric method has been found to give fairly good results. We believe it to be the best available rapid method for the estimation of soft resins suitable for commercial use. Gravimetric and volumetric determinations made on aliquots from the same solution of soft resins show that the volumetric method does not always agree with the gravimetric, often giving results which are somewhat higher. The comparative results of a number of determinations made in this manner from different samples of hops are as follows:

Soft resins, Authors' gravimetric method. Per cent.	Soft resins, Lintner's volumetric method. Per cent.
17.29	17.30
17.75	18.20
14.44	15.00
16.45	17.70
16.64	17.00
15.52	16.70
16.13	16.00
15.58	16.20

The slightly higher results given by the volumetric determinations are perhaps due to the use of the higher of the molecular weights of the different soft resins for making the calculations.

Drying the resins at as high a temperature as 80°

TABLE III.—TOTAL RESINS IN INDIVIDUAL HOP CONES.

Sample.	Cone I. Weight of cone in grams.	Cone I. Per cent. total resin.	Cone II. Weight of cone in grams.	Cone II. Per cent. total resin.	Cone III. Weight of cone in grams.	Cone III. Per cent. total resin.	Cone IV. Weight of cone in grams.	Cone IV. Per cent. total resin.	Cone V. Weight of cone in grams	Cone V. Per cent. total resin.	Cone VI. Weight of cone in grams.	Cone VI. Per cent. total resin.	Maximum per cent. total resin.	Minimum per cent. total resin.	Average per cent total resin.
1	0.2912	20.74	0.2753	21.57	0.2708	18.35	0.1800	18.88	0.1622	19.05	0.1322	17.70	21.57	17.70	19.38
2	0.2513	18.74	0.3105	20.03	0.3410	18.59	0.2088	22.41	0.1493	21.43	0.1870	20.59	22.41	18.59	20.29
3	0.4943	20.00	0.3075	23.22	0.3035	16.34	0.3630	18.07	0.3335	19.88	0.2064	18.12	23.22	16.34	19.27

C. is open to objection for two reasons: first, the resins turn brown at this temperature and undoubtedly there is some change in composition; second, a constant weight cannot be obtained. When the resins are dried *in vacuo* there is no evidence of much change in composition and when completely dried there is practically no change in weight.

Great care should be taken in securing petrolic ether of suitable quality for the extraction of the soft resins. The practice in this laboratory is to make two distillations, starting with the commercial product sold by dealers (boiling point 40–60°) and each time taking the fraction distilling over under 45° C.

Acknowledgment is due Mr. B. Pilkington for valuable assistance given in making some of the analytical determinations given in this paper.

CONCLUSIONS.

1. A comparative study has been made of some of the present methods used for the determination of hard and soft resins in the hop and their defects pointed out.

2. A method has been proposed by the authors which they believe overcomes some of the objections to present methods.

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THE CHEMISTRY OF ANAESTHETICS, IV: CHLOROFORM.[1]

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The career of chloroform has been chequered ever since its discovery, but especially since it has been used as an anaesthetic. The reasons for this are made apparent in this paper.

The report of this investigation has been subdivided as follows:

I. HISTORY.
II. USES.
III. MANUFACTURE: 1. *From Ethyl Alcohol.* 2. *From "Methylated Spirit."* 3. *From Acetone.* 4. *From Methane (Natural Gas).* 5. *From Carbon Tetrachloride.* 6. *Special Chloroforms of Foreign Manufacture.*
IV. PURIFICATION.
V. THE PHYSICAL CONSTANTS OF CHLOROFORM: 1. *Specific Gravity.* 2. *Boiling Point.*
VI. THE DECOMPOSITION OF CHLOROFORM: 1. *The Changes which Chloroform Undergoes upon Exposure to Air.* 2. *The Changes which Anaesthetic Chloroform Undergoes when a Current of Oxygen is Conducted through it.* 3. *The Decomposition of Chloroform Vapor upon Exposure to Gas Light, etc., during Administration.* 4. *The Effect of Agitation upon Anaesthetic Chloroform.* 5. *The Preservation of Chloroform.* 6. *The Storage of Anaesthetic Chloroform.*
VII. THE IMPURITIES OF ANAESTHETIC CHLOROFORM: 1. *Chemical Considerations.* 2. *Physiological Considerations.*
VIII. THE EXAMINATION OF ANAESTHETIC CHLOROFORM: 1. *The Tests for Odor.* 2. *Residue.* 3(*a*). *The Test with Sulphuric Acid.* 3(*b*). *The Test with Formalin—Sulphuric Acid.* 3(*c*). *Discussion of* 3(*a*) *and* 3(*b*). 4. *The Detection of Water in Chloroform.* 5. *The Detection and Estimation of Alcohol in Chloroform.* 6. *The Detection of Acetone in Chloroform.* 7. *The Detection of Methyl Alcohol and other Methyl Compounds in Chloroform.* 8. *The Detection of Ethyl Ether in Chloroform.* 9. *The Detection of Acetaldehyde in Chloroform.* 10. *The Determination of the Acidity of Chloroform.* 11. *The Decomposition Products of Pure Chloroform.* 11(*a*). *The Detection of Carbonyl Chloride.* 11(*b*). *The Detection of Hydrochloric Acid.* 11(*c*). *The Detection of Chlorine.* 12. *The Detection of Chlorine Substitution Products.* 12(*a*). *"Chlorinated Decomposition Products."* 12(*b*). *The Occurrence of Ethyl Chloride in Chloroform.* 12(*c*). *The Occurrence of Ethylene Chloride in Chloroform.* 12(*d*). *The Detection of Carbon Tetrachloride.* 13. *Scheme for the Examination of Chloroform for Anaesthetic and Analytical Purposes, with Particular Reference to the Detection of Avoidable Impurities.* 14. *The Degrees of Purity of American Chloroforms.*

In this paper the grades of chloroform have been discriminated in accordance with the following classification, which the authors propose as a basis:

A. *Pure Chloroform.*—Absolute chloroform—chloroform free from alcohol and all impurities.

B. *Anaesthetic Chloroform.*—Chloroform complying with the pharmacopoeial requirements. Such chloroform contains ethyl alcohol (up to 1 per cent.) and small amounts of water.

C. *Commercial Chloroform.*—Chloroform which contains at least 99 per cent., by weight, of absolute $CHCl_3$, but which may contain small amounts of "organic impurities."[1]

D. All other grades of chloroform should be classed as *impure commercial chloroform.*

E. The purity demanded of *laboratory chloroform,* or chloroform intended for analytical purposes, is entirely dependent upon the purpose for which it is intended. For ordinary reagent purposes, the grade specified under *anaesthetic chloroform* is suitable, and in general may be said to answer all such purposes; but in special cases *pure chloroform* may be required, and, when this is the case, it should always be prepared immediately before use, according to a method to be described in Section V, 1, A of this paper.

I. HISTORY.

Chloroform was discovered in 1831, yet it has been asserted that there are indications of an earlier acquaintance with the compound. For example, we are told by Hutman,[2] on the authority of Johannes Porta[3] and Sir Walter Scott,[4] that chloroform was known in former times and was then employed as a means of producing insensibility. Investigation shows that this statement is based upon misinterpretation.[5]

[1] Read at the regular June meeting of the New York Section of the American Chemical Society, 1911.

[1] See Section VII, 1, of this paper.

[2] *J. chim. med.*, [3] **4**, 476.

[3] "Magia Naturalis," 1619. It should be mentioned here that in 1589 Giaubattista Porta used an essence made from hyoscyamus, solanum, poppy, and belladonna, enclosed in a lead vessel, for producing sleep by inhalation of the vapor.

[4] "Letters on Demonology and Witchcraft," 1830.

[5] Most ancient authors who pretend to treat of the wonders of "Natural Magic," give recipes for calling up phantoms by the inhalation of certain gases from burning medicated mixtures, generally of oils, and by the use of suffumigations of strong herbs (Hibbert's "Apparitions," p. 120). The ancient Egyptians, Assyrians, and Chinese were familiar with many vegetable substances (*e. g., cannabis indica*) capable of producing ecstatic, sedative and anodyne effects (Snow's "Chloroform and Other Anaesthetics." 1858; Bernard's "Leçons sur les Anesthesiques et sur l'Asphyxie," 1875;

Silliman[1] confused chloroform with ethylene dichloride, stating that it had been "long known to chemists under the name of 'oil of the Dutch chemists' and 'Dutch oil,' from its discovery in 1796 by an association of Dutch chemists."

In 1831, Liebig[2] obtained chloroform by the action of a water solution of potassium hydroxide on chloral and by treating acetone with bleaching-powder. Almost at the same time, however, Soubeiran[3] obtained chloroform by the action of bleaching-powder on dilute alcohol, terming the product "ether bichlorique," and he was regarded as the discoverer of the compound until Liebig[4] advanced his claim as having been the first to prepare it, although he originally believed the substance to be a new chloride of carbon. According to some authorities,[5] Samuel Guthrie, an American, discovered chloroform simultaneously with Liebig and Soubeiran, and it has also been stated[6] that his discovery antedates that of Liebig several months. Silliman[7] stated in 1848 that "the production of 'chloric ether' so called, by the action of alcohol with bleaching-powders, was discovered almost simultaneously and without conference by our ingenious countryman, Samuel Guthrie, of Sackett's Harbor, New York, and by M. E. Soubeiran in France."

Liebig considered that he had prepared carbon trichloride whereas he actually obtained chloroform, and Guthrie confused his product with ethylene chloride; in both cases, the investigations were made in 1831 and published in the early part of 1832. Guthrie prepared chloroform without knowledge of the work of Liebig or Soubeiran, and is fully entitled to be credited with its independent discovery.[8]

Dumas,[1] in 1834, showed that chloroform contains hydrogen, and later he determined its true formula.[2] Dumas obtained chloroform by boiling tri-chloro-acetic acid with aqueous alkalies, and it was he who gave the compound its present name.[3] Regnault[4] proved that chloroform is the second substitution-product of methyl chloride; he termed it "ether hydrochlorique de methylene bichlorure." Berzelius referred to chloroform as "formylsuperchlorid," and Mitscherlich as "chloratherid."

II. USES.

Chloroform (methenyl trichloride; trichloro-methane; "formyl trichloride") is a colorless, limpid liquid possessing a sweet but somewhat burning taste and an agreeable characteristic odor. When pure, it is not combustible,[5] but when mixed with alcohol it burns with a smoky flame edged with green. Chloroform is slightly soluble in water (0.822 gram in 100 grams at 20°) and it imparts to it a sweet taste. It is miscible in all proportions with absolute alcohol, ether, benzene, and petroleum spirit. It is soluble to a limited extent in aqueous alcohol. It may be made into an emulsion with water by means of saponin.[6]

Chloroform is used in medicine[7] as an anaesthetic,[8] stimulant,[9] antispasmodic,[10] antiseptic,[11] analgesic,

Lyman's "Artificial Anaesthesia and Anaesthetics," 1883; and Dastre's "Les Anesthesiques," 1890). From the *Odyssey* (**4**, 220) we learn that Helen "cast a drug into the wine whereof they drank, a drug to lull all pain and anger and bring forgetfulness of every sorrow." Herodotus refers to the custom of the Scythians of inhaling the fumes of a kind of hemp; Dioscorides (*De Med. Mat.*, **4**, 76) makes mention of the practice of boiling in wine the root of the "*Atropa Mandragora*" and of administering some of the decoction prior to surgical operations; and Pliny (**35**, 94) refers similarly to the powers of the mandrake. Mandragora appears to have been used to some considerable extent (*Galen, lib.* **7**, 207; Lucian, "Demosthenes' Encomium," p. 36); it was employed in compounding the "spongia somnifera" of Theodoric. The Bible and the Talmud also contain references to ancient practices of inducing sleep by artificial means. However, excepting the use of Memphis marble and vinegar as a local anaesthetic by the Romans, carotid compression and (later) mesmerism, vegetable narcotics only were used to assuage suffering and for the induction of unconsciousness until the foreshadowing of the modern system of anaesthesia by the discovery of nitrous oxide.

[1] *Am. J. Sci.*, [2] **5**, 240.

[2] *Pogg. Ann.*, **23**, 444; *Ann.*, **1**, 31, 198.

[3] *Ann. chim. phys.*, [2] **48**, 131; *Ann.*, **1**, 272; Soubeiran and Mailhe, *Ann.*, **71**, 225.

[4] *Ann.*, **162**, 161.

[5] *E. g.*, Wurtz Flagg, "Ether and Chloroform," **1851**, p. 18; and Turnbull, "Anaesthetic Manual," **1879**, p. 87.

[6] *Pop. Sci. Mon.*, **12**, 738.

[7] *Loc. cit.* See Silliman, *Am. Chemist*, **5**, 86, for a full account of Guthrie's discovery.

[8] The attention of Guthrie appears to have been directed to the preparation of "chloric ether" by reading a passage in a work by Silliman ("Elements of Chemistry," **2**, 20), wherein it was stated that the alcoholic solution of "chloric ether" is of medicinal value. By the term "chloric ether" Silliman referred unmistakably to ethylene chloride, which Guthrie considered he had prepared in "spirituous solution," by the action of chloride of lime on alcohol of density 0.844, whereas he actually obtained an alcoholic solution of chloroform (*Am. J. Sci.*, [1] **21**, 64). Silliman, commenting on Guthrie's original contribution (*Ibid.*, 408), stated that "we cannot say precisely what takes place during the distillation of alcohol from chloride of lime. It is, however, worthy of notice that, as alcohol is believed to be composed of olefiant gas and water....and as chloric ether has been heretofore produced by the combination of chlorine and olefiant gas, it seems hardly to admit of a doubt, that in distilling alcohol from chloride of lime, the latter gives its chlorine to the olefiant gas of a part of the former, and thus produces chloric ether, which passes over, in solution, in another portion of the alcohol, while the water of that portion of the alcohol which afforded the olefiant gas, or the water which may be supposed to be produced by a combination of the elements, is detained by the lime." The question was raised, "Can any method be devised by which the alcohol can be detached from the chloric ether, and the latter obtained concentrated and in quantity?" Guthrie later (*Ibid.*, **22**, 105; see also, Hayes, *Ibid.*, 163) found that this could be accomplished by distillation over sulphuric acid, and obtained an "ether" possessing a density of 1.486 and boiling at 166° F. In a communication to Silliman, he stated that "as chloric ether is said to have a specific gravity of only 1.22 at 45°, a boiling point at 152° F., and to be decomposed by sulphuric acid, evolving chlorine, you may have good reason to doubt the purity of my product or the accuracy of my estimate, but you can very readily verify the first, and I shall be found to be very near the truth with the latter."

[1] *Ann. chim. phys.*, [2] **56**, 115; *Ann.*, **32**, 113.

[2] *Ann. chim. phys.*, [2] **71**, 353.

[3] *Ibid.*, [2] **56**, 120. To quote Dumas: "La formule.....correspond a un chlorure d'hydrogene carbone, qui est l'equivalent de l'acide formique anhydre.....C'est ce qui m'engage a la designer sous le nom de chloroforme."

[4] *Ann. chim. phys.*, [2] **71**, 377; *Ann.*, **33**, 328; *J. prakt. Chem.*, **19**, 210.

[5] See Ommeganck, *Am. Chemist*, **5**, 292.

[6] *J. Soc. Chem. Ind.*, **1887**, 382.

[7] Seyffarth (*Z. f. Arbeiter-Wohlfahrtseinrichtungen*, **10**, 319; see also *Chem. Ind.*, **27**, 379) has recommended the proposal of Weiskopf to use chloroform in cases of inhalation of nitrous fumes. Chloroform is used internally in colic, gastralgia, asthma, spasmodic coughing, atonic quinsy, hysteria, scarlet fever, neuralgia, cancer, hiccough, tic douloureux, etc.; and as an anaesthetic by inhalation in surgical operations. Externally, chloroform is used in a 20–50 per cent. liniment for rheumatism, neuralgia, colic, etc. It is used hypodermically in hydrocele. The maximum dose is 2 cc., and the usual dose is 0.6–1.3 cc. in solution.

[8] Sir James Simpson, "New Anaesthetic," **1847**, p. 7; *Illustrated London News*, December 4, 1847, 370/2. E. B. Simpson, *Century*, **25**, 412; *Liv. Age*, **66**, 720; *Mon. J. Med. Sci.*, September, 1847; Ednb. Medico-Chir. Soc., November 11, 1848. J. Y. Simpson's "Anaesthesia," **1849**, pp. 93, 145, 182, 193, 203. Chloroform of the density 1.48 was used by Simpson in 1847.

[9] Formby (1845) mentioned this use of chloroform. See also, Simpson, *Mon. J. Med. Sci.*, December, 1847. Guthrie published an account of the therapeutic effects of chloroform as a diffusible stimulant in 1832.

[10] Guillot proposed chloroform as an antispasmodic (*Ann. Thérap.*, **1844**, p. 35).

[11] As an antiseptic, chloroform prevents the growth of microörganisms,

counter-irritant, rubefacient, and as an antidote in cases of strychnine poisoning.

Anaesthetic chloroform, but more generally "technical" or "commercial" chloroform, is used technically (in electrotechnics, rubber industry, and photography) and in dentistry as a solvent. Chloroform is an important technical solvent; it dissolves fats, resins, one constituent part of caoutchouc, sulphur, phosphorus, iodine, many alkaloids and alkaloidal salts, as well as many other carbon compounds.[1]

Reagent chloroform is generally of the density 1.48–1.489, and is employed as a solvent, for testing primary amines, for the detection of aniline, etc. Its most extensive use as a solvent in the laboratory is for dissolving alkaloids.

396,540 pounds of chloroform, valued at $98,070, were produced in the United States in 1900; of this amount, 334,000 pounds were produced in New Jersey, and 62,540 pounds in New York. In 1905, 616,670 pounds, valued at $165,604, were manufactured in this country.

III. MANUFACTURE.[2]

1. From Ethyl Alcohol.

A. Soubeiran[3] showed that chloroform is formed by the action of bleaching-powder on dilute alcohol.[4]

When alcohol of various strengths is poured upon bleaching-powder, the distillate affords an oil which may be separated by fractionation. The amount of chloro-acetal (b. p., 150–160°) is therefore greatly diminished by diluting the alcohol.[5]

The theory of the process sometimes given is as follows: The bleaching-powder is supposed first to convert the alcohol into chloral, and then the lime which is present, or which is formed, splits this into calcium formate and chloroform.[6]

$$8CaO.Cl_2 + 2C_2H_5OH = 2C_2Cl_3HO + 5CaCl_2 + 3CaO + 5H_2O =$$
$$2CCl_3H + Ca(CHO_2)_2 + 5CaCl_2 + 2CaO + 4H_2O.$$

Dott,[1] however, stated that the formation of chloroform from ethyl alcohol is best indicated by

$$3C_2H_5OH + 8Ca(OCl)_2 = 2CHCl_3 + 3CaCO_3 + CO_2 + 8H_2O + 5CaCl_2.$$

Dott confirmed the observation of Finnemore[2] and Wade that a small proportion of ethyl chloride is formed in preparing chloroform from ethyl alcohol.[3]

B. According to the process of Schering,[4] halogen salts of the alkalies or alkaline earths are electrolyzed in the presence of alcohol, acetone or aldehyde in a warm aqueous solution, carbon dioxide being passed continuously into the electrolyte during the process.

Kempf[5] invented a process for the manufacture of chloroform by electrolyzing suitable halogen compounds of the alkalies and alkaline earths in alcoholic solution with constant heating; and Trechcinski[6] prepared chloroform by the electrolysis of an aqueous-alcoholic solution of calcium chloride. The latter used platinum electrodes and the calcium chloride solution was contained in a glass vessel; the gases and chloroform vapor were conducted off through a tube to an absorption apparatus. The yield was found to be increased when alcohol was added to the spent electrolyte solution.

Although ethyl alcohol was formerly used for the production of chloroform, it is now largely, and almost entirely, replaced by acetone, and more recently carbon tetrachloride has become an important source.

2. From "Methylated Spirit."

Pure methyl alcohol does not yield chloroform when treated with bleaching-powder, although it is formed from commercial methyl alcohol.[7] "Methylated chloroform," at one time extensively used in England, is chloroform prepared from wood spirit ("methylated spirit.")[8] It is incorrect to suppose that "methylated chloroform" has received an actual addition of wood spirit, but such chloroform is liable to be much less pure than that obtained solely from ethyl alcohol. According to Allen,[9] chloroform prepared from "methylated spirit" is more difficult to purify than that made from ethyl alcohol, but a product has been manufactured in England from the former source which appears to be equal in all respects to the more expensive article.[10]

but it does not affect the action of soluble ferments (*J. Soc. Chem. Ind.*, **1886**, 331). On the antiseptic applications of chloroform, see Robin, *Compt. rend.*, **30**, 52; Augendre, *Ibid.*, **31**, 679; Barnes, *Pharm. J.*, [3] **5**, 441; Salkowski, *Chem. Repert.*, **1888**, 166; and *Pharm. J.*, [3] **18**, 315, 356, 855. Chloroform may be used as a preservative of mucilage and infusions. Munz (*Pharm. J.*, **1875**, 967) proposed the use of chloroform as a test between chemical and living ferments.

[1] See, in this connection, Pettenkofer, *Jahresber.*, **1858**, 363; Schlimpert, *Ibid.*, **1859**, 405; Nowak, *Archiv. Pharm.*, [3] **3**, 281; Hesse, *Pharm. J.*, [3] **4**, 649. For a list of substances soluble, insoluble, and partly soluble in chloroform, see *Am. J. Pharm.*, **1852**, 147.

[2] Only methods of commercial importance are considered.

[3] *Loc. cit.*

[4] See also, Bechamp, *Ann. chim. phys.*, [5] **22**, 347. This process is usually conducted as follows: Bleaching-powder (40 parts), water (100–150 parts), alcohol (4–10 parts), and slaked lime (4–10 parts) are distilled together; the distillate separates in two layers, the lower one being chloroform, which is then purified. For papers on the manufacture of chloroform from alcohol and "chlorinated lime," see *Am. J. Pharm.*, **1862**, 25, 42; **1868**, 289. In *Chem. Ztg.*, **10**, 338, is described the process used in Germany in 1886; in Gray's "Supplement to the Pharmacopoeia," **1846**, p. 633, is described the process in general use in 1845; and in *Sci. Am.*, **95**, 421, the French process is given by Boyer. On the manufacture of chloroform from bleaching-powder and ethyl alcohol, see especially Frerichs, Am. Inst. of Chem. Eng., 1911.

[5] Goldberg, *J. prakt. Chem.*, **132**, 111. On the preparation of chloroform from alcohol, see, in addition, Soubeiran, *Compt. rend.*, **25**, 799; Meurer, *Chem. Centr.*, **1848**, 154; Carl, *Ibid.*, **1848**, 236; Larocque and Hurault, *N. J. Pharm.*, **13**, 97; Siemerling, *N. Br. Arch.*, **53**, 23; Kessler, *N. J. Pharm.*, **13**, 162; Ramdohr, *N. Br. Arch.*, **83**, 280; Hirsch, *Ibid.*, **107**, 137. The alcohol used should not contain fusel oil (Regnault and Hardy, *J. Pharm. Chim.*, [4] **30**, 405) or higher alcohols.

[6] Watts' "Dictionary of Chemistry," **2**, 68 (1890).

[1] *J. Soc. Chem. Ind.*, **27**, 6, 271.

[2] *J. Chem. Soc.*, **85**, 938.

[3] See *ethyl chloride*, Section VIII, 12(*b*).

[4] German Patent 29,771, 1884; *Ber.*, **17**, ref. 624. Also, Dony-Henault, *Z. Elektrochem.*, **7**, 57, Wäser, *Chem. Ztg.*, **34**, **141.**

[5] English Patent 8,148, 1884; German Patent 29,771, 1884; French Patent 162,306, 1884; Belgium Patent 65,227, 1884.

[6] *J. Russ. Phys.-Chem. Soc.*, **38**, 734; *Pharm. Ztg.*, **51**, 523.

[7] Belohoubek, *Ann.*, **165**, 349.

[8] "Methylated spirit" is a mixture of rectified spirit with 10 per cent. of wood naphtha; it has been used in the manufacture of chloroform, owing to its being obtained duty-free (Thorpe).

[9] "Commercial Organic Analysis," **1**, 235 (1908). Although "methylated chloroform" is not on the American market, contamination with *methyl alcohol* is considered under that caption.

[10] Allen is also authority for the statement that imperfectly purified "methylated chloroform" is specifically lighter than the pure substance, has an empyreumatic odor, and produces disagreeable sensations when inhaled. In some cases, we are told, such chloroform appears to be actually poisonous and produces general and rapid prostration. Such chloroform contains several units per cent. of a chlorinated oil, lighter than water and boiling at a much higher temperature than chloroform. A similar but different oil (heavier than water) has been detected in much smaller quantity

Gregory[1] found that the chloroform prepared from ethyl alcohol and wood spirit, when fully purified, is quite identical in all its properties, but that from the former is more easily purified. In fact, it may be asserted on the authority of Brown, Squibb, Schacht and Biltz[2] that properly purified chloroform is the same from whatever source it is obtained; however, Cross and also Spilsbury[3] have expressed the opinion that chloroform made from ethyl alcohol is physiologically safer than that from methylated spirit and acetone. The latter opinion is a recent one (1909) and is substantiated, at least in part, by other evidence, but is totally incorrect when the chloroform is properly purified.[4]

3. *From Acetone.*

A. The preparation of chloroform from acetone was referred to by Liebig in 1832. Böttger, in 1848, showed how to prepare chloroform from acetates and from acetone, and stated that chloroform made from acetone directly was then to be had on the market, one ounce of acetone yielding 1¼ ounces of chloroform. The reason why this method of preparation was not generally followed up was doubtless attributable, as indicated by Squibb,[5] to the erroneous statements of Siemerling (1848) and Wackenroder, adopted by such authorities as Gmelin and Watts, who for some reason failed to obtain anything like the proportion mentioned by Böttger. Thus, Watts[6] stated, in 1874, that the manufacture of chloroform from acetone cannot be advantageously carried out, since the price of acetone is high and it yields only about one-third of its weight of chloroform when treated with chloride of lime. However, it may be shown that Siemerling used only about half of the theoretical proportion of chloride of lime, and that he apparently made no attempt to recover and treat again the acetone left unconverted.

Orndorff and Jessel[7] found that the products formed by the action of bleaching-powder on acetone are chloroform, calcium hydroxide, calcium chloride, and calcium acetate. They considered it probable that the first action of the bleaching-powder is a substituting one, yielding trichloracetone or methyl chloral, and that this is then acted on by calcium hydroxide formed at the same time, giving chloroform and calcium acetate:

$$2CH_3COCH_3 + 6CaOCl_2 = 2CHCl_3 + 2Ca(OH)_2 + 3CaCl_2 + Ca(C_2H_3O_2)_2.$$

Dott, however, states that the equation

$$2CO(CH_3)_2 + 3CaOCl_2 = 2CHCl_3 + (CH_3.CO_2)_2Ca + 2Ca(OH)_2$$

in chloroform prepared from alcohol containing no methyl compounds; these oils may be totally eliminated by purification of the crude chloroform.

[1] *Mon. J. Med. Sci.*, May, 1850; *Pharm. J.*, **9**, 580.

[2] *Pharm. J.*, [3] **24**, 811.

[3] *Ibid.*, [4] **29**, 660.

[4] It has also been stated that headache frequently occurs among workmen while bottling chloroform made from methylated spirit, whereas the symptoms were not observed while manipulating chloroform derived from ethyl alcohol (*Ibid.*, [4] **18**, 515).

[5] *J. Am. Chem. Soc.*, **1896**, 231.

[6] "A Dictionary of Chemistry," **1**, 918. This statement was based on the results of Siemerling (*Arch. Pharm.*, [2] **53**, 23).

[7] *Am. Chem. J.*, **10**, 366. Dott (*Pharm. J.* **81**, 54) found that there are also considerable amounts of calcium carbonate and chlorate in the residual liquor obtained in preparing chloroform from acetone.

agrees well with his experimental results. This presentment of the reaction may be taken as representative.

B. Michaelis,[1] and Michaelis and Mayer[2] invented a process wherein rude acetates are subjected to dry distillation at high temperatures to remove the fluid products therefrom, which are then subjected to the action of a hypochlorite and the chloroform produced is condensed; the residual products of the dry distillation are converted into acetic acid or purified acetates. This process is used by an American firm.

C. Rumpf[3] devised this process for the manufacture of chloroform from acetone:—acetone in a dilute state is periodically introduced into the bottom of a still containing chloride of lime solution, with agitation of the solution. The chloride of lime employed is more than five times the weight of the acetone, resulting in the chloroform produced equaling the acetone in volume. Rumpf based his patent upon the incorrect quotation from Watts. Squibb, to avoid litigation, and partly because he found that by taking an excess of acetone the hypochlorite is more economically and promptly utilized, and the resulting chloroform purer, while the unconverted acetone is easily recovered and again treated, proposed to use Siemerling's proportions, and to conduct the whole operation in an apparatus described by himself in 1857, and used for many years in the production of chloroform from alcohol.

In the process of Porsch,[4] vapors from the dry distillation of an acetate, and chlorine gas, are continuously discharged, in opposite directions, under pressure, in an aqueous bath of an alkaline earth, as milk of lime, subjected to heat; the hydrochloric acid is separated from the resultant vapors and the chloroform vapors are condensed.

According to the patented process of Chute,[5] wood spirit, containing ketonic impurities such as acetone, is treated with a hypochlorite, and the chloroform, which is thus produced, is isolated by diluting the reaction mixture with water, or with a saline solution, and then distilling off the chloroform.

D. Chloroform is now made from sodium chloride and acetone by electrolysis.[6] However, there appears to be a strong prejudice in the pharmaceutical trade against chloroform from this

[1] U. S. Patent 322,194, 1885.

[2] English Patent 8,523, 1885; German Patent 36,514, 1886.

[3] U. S. Patent 383,992, 1888. On the patents of Rumpf for the production of chloroform by the "acetone process," see Sadtler, *Pharm. Era*, **1889**, 376. Sadtler stated that the chloroform thus obtained is quite free from chlorinated side-products, but is nevertheless purified by treatment with sulphuric acid and careful washing, and then brought exactly to the pharmacopoeial standard.

[4] U. S. Patent 573,483, 1896.

[5] U. S. Patent 893,784, 1908.

[6] In 1900, the following process was described (*Rev. Prod. Chim.*, **3**, 309): A 20 per cent. solution of sodium chloride is heated at 100° C. in a leaden still, and is kept agitated by means of carbon spatulas, which, at the same time, serve as anodes for the (5–6 ampere) current. Acetone is introduced into the bottom of the still and combines with the liberated chlorine to form acetone trichloride, which, in the presence of the sodium hydroxide, is decomposed with the formation of sodium acetate and chloroform. The latter is conveyed through a condenser and is collected in a suitable receiver. The yield was found to be 180 parts out of 210 theoretically possible. Klar (*Chem. Ind.*, **19**, 159) has also described the process for the preparation of chloroform in which acetone is chlorinated by chlorine evolved during the electrolysis of a 20 per cent. sodium chloride solution. Teeple (*J. Am. Chem. Soc.*, **26**, 536) has discussed very fully the electrolytic preparation of chloroform from acetone. He found that the conditions necessary for the successful preparation of chloroform by the electrolysis of a chloride in the presence of acetone are: A temperature below 25° C., absence of alkali, a high current density at the cathode and a low one at the anode. A good yield of chloroform may also be obtained by the action of chlorine upon calcium hydroxide solution containing acetone. This suggests that the electrolysis of a calcium chloride solution in the presence of acetone would be the best method of making chloroform, provided the high resistance of the deposits on the anode could be overcome. The process of Schering (1884), already referred to, specifically initiated the efforts which have been made to devise a satisfactory process for the production of chloroform from acetone electrolytically. See also, *Rev. Scien.*, Feb., 1893.

source, which causes the manufacturers to be reluctant about divulging any information concerning the process.

When acetone is used for the preparation of chloroform, it should be previously purified[1] and this purification should be carefully conducted in order to prevent the formation of condensation compounds.[2]

It has been stated that chloroform made from acetone is not nearly so good an anaesthetic as chloroform made from ethyl alcohol;[3] but this opinion is based upon the findings of Wade and Finnemore,[4] that chloroform prepared from ethyl alcohol contains a very small proportion of ethyl chloride. When chloroform is properly made from purified acetone, careful purification will result in the production of pure chloroform.[5]

Chloroform is now being manufactured from acetone by at least three firms in this country,[6] while anaesthetic chloroform prepared from crude chloroform from this source is being marketed with success by at least five manufacturing chemists.

4. From Methane (Natural Gas).

A. About 490,000,000,000 cubic feet of natural gas, valued at approximately $71,000,000, are produced annually in the United States. In Pennsylvania, for example, many wells of 5,000,000 cubic feet daily capacity have been drilled. This gas contains 50–95 per cent. of methane,[7] and, bearing in mind the demonstration of Regnault[8] that chloroform is formed by the action of chlorine on methane in daylight and ultimately in sunlight, several investigators have sought to effect a chlorination in order to obtain substitution products. The ultimate object has been to produce a constant yield of an intermediate product.

B. In 1879, Mallet[9] proposed passing chlorine and methane through a body of porous material not acted upon by the chlorine, as prepared carbon, meanwhile maintaining the temperature between 30° and 90° C.

C. Later, Colin[1] made serious endeavors to manufacture and separate the chlorides of methane by the mutual combustion of chlorine and natural gas, mixed in suitable proportions within a retort. The gases were ignited and the reaction was maintained by an electric spark of proper tension, the chamber being kept at a proper temperature. After absorbing the hydrogen chloride from the product, the methyl chlorides were liquefied and attempts were made to thereby separate them. An experimental plant was installed for manufacturing chloroform from natural gas by this process at Allegheny, Penn.

Without discussing the suitability of the provisions made for the reactions in these two processes, it may be remarked that both were unsuccessful, mainly owing to the tendency of the methane, when chlorinated, to constantly produce either methyl chloride or carbon tetrachloride, as shown by Phillips.[2] The latter found that dichlormethane and chloroform are formed in relatively small quantities, and concluded that the manufacture of chloroform from natural gas, as indicated by his experiments, is likely to prove a difficult matter.[3]

D. The process of Elworthy for the manufacture of chloroform from methane is a decided improvement over the older ones, although future application only can decide its fate. In conjunction with Lance, Elworthy[4] prepared methane by the synthetic method of Sabatier and Senderens,[5] by passing a mixture of water-gas and hydrogen over heated nickel at 190–250° C.—one of the convenient methods of preparing methane, although any excess of carbon monoxide greatly retards the reaction. Elworthy and Lance passed methane properly mixed with chlorine through a series of thick-walled glass tubes exposed to direct or diffused sunlight, the light from an electric arc, etc., and their patent specifies dilution of the gases to avoid explosion.[6]

E. Pfeifer and Szaroasy[7] have recently claimed a process for the production of halogen derivatives of hydrocarbons, consisting in treating methane with a halogen, or with a compound which liberates free halogen in the reaction chamber, under the action of the silent discharge.

We were informed that chloroform is now being made from natural gas by an American firm, and that such chloroform is known to the trade as "gas chloroform," but this appears to be incorrect, the source being carbon tetrachloride prepared from carbon disulphide and not methane.

[1] In *Am. J. Pharm.*, **1885,** 321, is an account of a method for purifying acetone used in the preparation of chloroform.

[2] Dott (*J. Soc. Chem. Ind.*, **27,** 272) has called attention to the importance of the impurities which may be present in commercial acetone. He found that samples which indicated 99 per cent. by the iodoform and other methods gave about 7 per cent. distilling above 58°. This was first thought to be due to the presence of higher ketones or other bodies yielding iodoform, but Gibson suggested that it might possibly be caused by the presence of even 1 per cent. of a mixture of the condensation products of acetone (*e. g.*, mesityl oxide, phorone, and mesitylene), which all have relatively high boiling points. It was found that on mixing pure acetone with 1 per cent. of the mixed condensation products it behaved on distillation and in its iodoform yield, and otherwise, like the samples referred to. When purifying acetone, therefore, manufacturers should avoid treatment with mineral acids or other method which is likely to cause formation of the condensation compounds. On the purity of acetone, see also Guttman, *Dingler's Polyt. J.*, **1894,** 96; Klar, *J. Soc. Chem. Ind.*, **1897,** 722.

[3] Price, *Pharm. J.*, **23,** 89.

[4] *Loc. cit.*

[5] J. F. MacFarlan & Co. (*The Lancet*, **1905,** i, 747) have expressed the opinion that chloroform prepared from acetone is by no means generally accepted as inferior to chloroform prepared from alcohol, and consider that up to the present, insufficient evidence has been adduced to establish the view that it is actually inferior.

We may state here that, from our experience, anaesthetic chloroform manufactured from acetone has been found by American anaesthetizers to be fully as satisfactory as that from other sources.

[6] The manufacture of chloroform from acetone has been carried on since 1885 in this country and since 1882 in Germany.

[7] Pennsylvania natural gas contains from 50–99 per cent. total paraffins; Ohio gas, 90–93 per cent.; and West Virginia gas, 80–87 per cent.

[8] *Ann. chim. phys.*, [2] **71,** 380. See also, Dumas, *Ann.*, **33,** 187; *Ann. chim. phys.*, [2] **73,** 95.

[9] U. S. Patent 220,397, October 7, 1879. Cf. U. S. Patents 880,900, March 3, 1908, and 1,009,428, November 21, 1911, of J. MacKaye.

[1] U. S. Patent 427,744, May 13, 1890.

[2] *Am. Phil. Soc.*, March 17, 1893.

[3] *Am. Chem. J.*, **16,** 362.

[4] French Patent 353,291, May 15, 1905. See, in this connection, German Patent 222,919, November 5, 1909, of J. Walter; and *Allg. Osterr. Chem. Ztg.*, **29,** 23.

[5] *Compt. rend.*, **134,** 9, 514.

[6] Elworthy's death four years ago occurred before his process had been commercially demonstrated, and we have been informed that it is now very doubtful if the process can or will be carried out.

[7] 12,058. D. Anm. P. 24,872, September 25, 1911.

5. From Carbon Tetrachloride.

Geuther found that chloroform results from the action of nascent hydrogen (from zinc and sulphuric acid) upon carbon tetrachloride;[1] and Damoiseau thought that chloroform might be profitably prepared by passing a mixture of methyl chloride and chlorine in the proper proportions through a long tube containing animal charcoal and heated between 250° and 350° C.[2] It was not until successful commercial processes for the production of carbon tetrachloride had been developed, however,[3] that it was ascertained that chloroform may be advantageously prepared from carbon tetrachloride.[4]

The carbon tetrachloride used is prepared from carbon disulphide (the electric furnace product), and manufacturers in the United States state that it is so free from sulphur compounds that "no part of the distillate separated from a batch of 5000 pounds through a long fractionating column will show any sulphur compounds by the most delicate tests known." The presence of carbon disulphide in the chloroform produced is guarded against by means of a process for removing carbon disulphide from the carbon tetrachloride used; when traces are present, the tetrachloride is fractionated in a high column still until the distillate will give no response with tests for the presence of carbon disulphide,[1] then the material remaining in the still is used for the manufacture of chloroform and the distillate is considered as commercial carbon tetrachloride, which is usually guaranteed to contain 99.7 per cent. of absolute CCl_4.

We have been informed that "technically pure" chloroform produced from disulphide tetrachloride may be recognized by its small content of carbon disulphide and carbon tetrachloride, and that such a grade also possesses a higher refractive index than other varieties. We have not examined any of this "technically pure" chloroform, but from our experience the anaesthetic grade conforms in full with the required pharmacopoeial standards.

6. Special Chloroforms of Foreign Manufacture.

Considerable quantities of chloroform are produced in Germany for domestic and foreign consumption.[2]

In addition to anaesthetic chloroform prepared by the action of bleaching-powder on alcohol and acetone (Chloroform *Gehe*, *Riedel*, *Merck*, *Kahlbaum*, *de Haen*, *Konig*, and *Cotta*), "Chloroform e Chloral," "Chloroform Pictet," and "Chloroform Anschütz" are found on the German market.

A. Chloral Chloroform.—Liebig found that chloroform might be prepared by distilling chloral with excess of aqueous potassium hydroxide, sodium hydroxide or baryta, or with milk of lime, repeatedly agitating the oily distillate with water, separating from the water as completely as possible by decantation, and then distilling with 6 or 8 times its volume of strong sulphuric acid in a perfectly dry apparatus. In 1870, chloral chloroform was sold under the name "English Chloroform" in Germany, and Hager, after an examination, expressed the opinion that chloroform from chloral was the purest then obtainable.[3]

The invention of Liebreich[4] for preparations for the production of chloroform relates broadly to a product consisting of a dry mixture of chloral hydrate and alkali, which may be compressed into any convenient shape; on treatment with water, chloroform is pro-

[1] *Ann.*, **107**, 212.

[2] *Compt. rend.*, **91**, 1071. See also, *Compt. rend.*, **92**, 42, 145; Vincent, *Jahresber. Chem. Technol.*, **1881**, 971.

[3] As early as 1834 it was learned that carbon disulphide may be converted into carbon tetrachloride by chlorination (Kolbe, *Ann.*, **45**, 41; **54**, 146. See also, Hofmann, *Ibid.*, **115**, 264; Klasow, *Ber.*, **20**, 2376; Moneyrat, *Bull. soc. chim.*, [3] **19**, 262; Serra, *Gaz. chim. ital.*, **29**, 353). Müller and Dubois (Eng. Patent 19,628, 1893) devised a process for the production of carbon tetrachloride by the addition of finely divided iron to a mixture of carbon disulphide and sulphur chloride; cf. Eng. Patent 13,733 of 1901, of Urbain, wherein practically the same process is claimed, and U. S. Patent 753,325, dated March 1, 1904, of A. W. Smith. On the preparation of carbon tetrachloride, see Margosches, "Der Tetrachlorkohlenstoff," **1905**, pp. 4 and 15.

[4] In 1896, the following method for the preparation of chloroform was described (*Chem. Rev.*, **1896**, 88): To 75 kg. of carbon tetrachloride are added, in the cold, 60 kg. of hydrochloric acid (22° B.) and 50 kg. of zinc, the whole being then heated in an autoclave. Hydrogen is liberated and reduces one atom of chlorine with the formation of hydrochloric acid which then attacks the zinc anew, and the cycle continues until the process is complete, a condition indicated by the formation of the hydrochloric acid. The upper layer of the substance is removed and the product refined. (See also, *Pharm. Centralh.*, **37**, 715; *Pharm. J.*, **57**, 377). "On the Preparation of Chloroform from Carbon Tetrachloride," see Gustavson, *Ber.*, **7**, 128; Eder and Valenta, *Chem. Ind.*, **20**, 249; *Pharm. Ztg.*, **41**, 22; Klar, *Chem. Ind.*, **19**, 159.

In 1902, A. W. Smith, of Cleveland, Ohio, devised a successful process of making chloroform from carbon tetrachloride. This process (*loc. cit.*) consists in the production of chloroform by the following steps: the action of heated sulphur upon heated carbon, so as to produce carbon disulphide; the action of chlorine upon sulphur, so as to produce sulphur chloride or dichloride; the action of sulphur chloride or dichloride upon carbon disulphide, so as to produce carbon tetrachloride; and, finally, the reduction of carbon tetrachloride, so as to produce chloroform. According to the specification of Smith, the reduction of the purified carbon tetrachloride to chloroform may be accomplished in a number of ways, "as by treating the tetrachloride with some substance or substances that will generate nascent hydrogen, such as an acid and a metal or an alkali and zinc or by electrolytic methods. This reaction may be much shortened in time by bringing the tetrachloride and acid used in the production of nascent hydrogen into more intimate contact with each other by the use of a mutual solvent for both tetrachloride and acid (ethyl or methyl alcohol)." Smith "found, however, that mechanical agitation of the tetrachloride with reducing substances answers the same purpose to a certain extent and is preferable".....and "that simple agitation of the tetrachloride with water and finely-divided iron without any acid or simply a trace of acid to start the reaction is one of the most efficient methods of reduction of the tetrachloride to chloroform," which "method is far cheaper than that involving the use of acids or most other reduction methods and possesses the added advantage that it can be readily controlled, so that little or no reduction to dichlormethane takes place." The process of Smith is in use by an American concern, and modifications have been put into effect and are now the subject of other patents under action. This company began the commercial manufacture of chloroform from carbon tetrachloride in 1902, and the present capacity is about 300,000 pounds per annum. At the present time, part of the product is being exported and is reported to be of satisfactory quality, complying with certain foreign pharmacopoeial requirements.

[1] The detection and estimation of *carbon disulphide* in chloroform will be referred to later.

[2] In 1910, for example, 161,900 kg. of chloroform and chloral were exported, 19,000 kg. of which went to the United States; the average price is from 170–180 marks per 100 kg.

[3] *Year Book of Pharm.*, **1870**, 119. Hager found that "English chloroform" was really chloral chloroform containing 0.75–0.80 per cent. of alcohol. The addition of pure sulphuric acid to this chloral chloroform caused no coloration, while it was found to color slightly the ordinary grade of chloroform then in use. Evaporation of some of the substance on a watch-glass in the air was found to afford another means of testing the substance. When all but a few drops had disappeared, the ordinary chloroform residue was found to possess a disagreeable odor, while the other retained its pleasant odor. Versmann (*Pharm. J.*, [3] **2**, 63) also found that the residue of chloral chloroform possesses no foreign odor.

According to a later writer, however (Ahrends, *Pharm. Ztg.*, **1891**, 263), German chloroform is generally superior to that manufactured in England. This is as one would now suspect, since the British Pharmacopoeia is considerably less stringent than that of Germany.

[4] Eng. Patent 15,930, 1904.

duced. The product of this process has been known as "Chloroform Liebreich," and "Chloroform-Schering," now on the American market, is prepared from Liebreich's crystallized chloral hydrate.

Langgaard[1] examined the eight principal brands of chloroform obtainable in Germany, and found that chloral chloroform was the purest. As a general rule, however, all of the German chloroforms of anaesthetic grade are of good quality,[2] and the grade at present prescribed by the *Arzneibuch* is, at least in most cases, equal to chloroform prepared from chloral. It has been also claimed that chloral chloroform does not undergo decomposition, but this has been shown to be incorrect;[3] in fact, like all the other pure preparations, "Chloroform e Chloral" decomposes if not preserved by the addition of, for example, a little alcohol.[4]

B. Chloroform Pictet.—This preparation is obtained by crystallization at —80° and then at —82°.[5]

Schacht[6] has shown that although the Pictet chloroform is a good preparation, that obtained from the purest crystallized chloral hydrate is quite equal to it, and like the latter it requires the addition of a preservative.

C. Chloroform Anschuetz.—More recently a special preparation under the name "Anschütz Salicylid Chloroform" or "Salicylchloroform" has been placed on the German market; it is obtained from a crystalline compound of salicylid, first prepared by Anschütz.[7] According to the patented process of the latter, chemically pure chloroform is produced by decomposing by heat double compounds of chloroform and lactid-like condensation products derived from "orthophenol carbonic acids," as salicylid, and then condensing the pure chloroform; salicylid-chloroform is prepared by boiling salicylid in chloroform,[8] and in this compound chloroform plays the same role as the water of crystallization in many crystalline salts, being obtained in a pure state by simple distillation therefrom.[9] Salicylid-chloroform is said to be extensively used by anaesthetists in Russia, since it conforms to the pharmacopoeia of that country, and it is especially recommended by others for anaesthesia.

The comparative prices of anaesthetic chloroform prepared from acetone by means of bleaching-powder, chloroform from chloral by potassium hydroxide, "Chloroform Pictet," and "Chloroform Anschütz," are respectively, taking the first as a basis, 1, 3, 6, and 10.

[1] *Therap. Monatsh.*, May, 1902.

[2] The results obtained by the authors in the course of an examination of the principal German products will be given later.

[3] See *Am. J. Pharm.*, **42**, 409.

[4] See Schacht, *J. Soc. Chem. Ind.*, **1893**, 543; also *Preservation.* It is said that the vapor from chloral hydrate separates with difficulty from the vapor of chloroform, and that it is impossible to prevent contamination.

[5] See *Purification*, where the process of Pictet is detailed.

[6] *Loc. cit.*

[7] *J. Soc. Chem. Ind.*, **1893**, 782. Cf. the analogous conduct of leprarin (Kassner, *Archiv. Pharm.*, **237**, 44). On $CHCl_3.18H_2O$, see *Z. anal. Chem.*, **25**, 118.

[8] U. S. Patent 535,270, 1895; German Patent 70,614, 1894.

[9] Anschütz, *Ann.*, **273**, 94; Arends, *Chem. Ind.*, **16**, 78. The purity of this chloroform will be referred to in succeeding pages.

IV. PURIFICATION.

The crude chloroform prepared by the action of bleaching-powder on alcohol, by the action of bleaching-powder on acetone,[1] or by the electrolysis of solutions of chlorides of the alkalies or alkaline earths in alcohol or acetone[2] is not of so high a degree of purity as that obtained by the action of alkalies on previously purified chloral, and requires more careful purification before it is suitable for anaesthetic purposes. The extent of the purification necessary is, of course, dependent upon the purity of the materials used as well as upon the process employed, but especially upon the purpose for which the chloroform is intended.

A. The earliest methods for the purification of crude chloroform consisted in washing the distillate with water to remove alcohol,[3] and then drying over calcium chloride, or sometimes rectifying without having previously dried the product. In 1848, the method was introduced whereby crude chloroform was purified by shaking with potassium hydroxide, drying over calcium chloride, and then rectifying; this method serves to remove chlorine[4] and acids, but only partially eliminates alcohol and other probable contaminants.

Gregory[5] purified chloroform by agitating it and leaving it in contact with sulphuric acid until the latter was no longer colored by it, then he removed the chloroform and placed it in contact with a small quantity of manganese dioxide to free it from "sulphurous acid." About 1860, the German custom was to rectify over concentrated sulphuric acid.[6] At the present time treatment with sulphuric acid is generally resorted to and forms the most important stage of the purification of crude chloroform prepared from alcohol or acetone. Pure concentrated sulphuric acid has no action on chloroform itself unless

[1] See *Pharm. J.*, [3] **20**, 84.

[2] See *J. Soc. Chem. Ind.*, **1885**, 243.

[3] When made from alcohol, crude chloroform contains considerable quantities of alcohol in solution, from which it may be separated by repeatedly washing with water. In order to wash a yield of 160–175 kg. of crude chloroform, about 800 liters of water are necessary to obtain anaesthetic chloroform, although this washing forms only one stage of the purifying process.

[4] Kessler (*J. Pharm. Chim.*, [3] **13**, 162) found that chloroform may be freed from chlorine by agitation with potassium hydroxide, and suggested that it be further purified by drying over calcium chloride and then rectification. It has been stated by Pictet (U. S. Patent 489,592, 1893) that when chloroform containing hydrochloric acid and chlorine is neutralized with an alkali, there remains in the chloroform thus treated a series of heterogeneous bodies "consisting essentially of the series of the tetrachlorides of carbon which remain dissolved in the liquor" and no reagent known at present can serve for their detection or elimination.

[5] *Proc. Roy. Soc. Ednb.*, **1850**, 391. According to Abraham (*Pharm. J.*, **10**, 24), chloroform, when thus purified, quickly decomposes, and is afterwards found to contain hydrochloric acid and free chlorine.

Guthrie, in 1832, found that "chloric ether may be entirely, or very nearly so, separated from alcohol by repeated rectification, from muriate of lime; it may thus be brought to the specific gravity of 1.44." However, "chloric ether, distilled off sulphuric acid, has a specific gravity of 1.486, or a little greater, and may be regarded as free from alcohol." He recommended that the "chloric ether" be finally washed with a concentrated solution of potassium carbonate.

[6] The United States Pharmacopoeia of 1850 gave a process for preparing chloroform; this was transferred in 1860 to the *Materia Medica Catalogue*. "Chloroformum venale," or commercial chloroform, was introduced and also a formula for purifying chloroform; this was dropped in the Pharmacopoeia of 1890.

the operation is unduly prolonged,[1] but it decomposes some of the impurities which are commonly present and removes others. In the next place, the product is brought in contact with sodium carbonate,[2] or it is washed with lime water and then dried over calcium chloride.[3] In any case, it should be finally distilled at a temperature not above 64°.[4]

One method of preparing anaesthetic chloroform from commercial chloroform manufactured from acetone, now in use by a prominent manufacturing chemist, consists in conducting the vapor of the commercial chloroform through concentrated sulphuric acid and then passing it through a tower containing crystallized sodium carbonate, after which treatment the purified chloroform is brought to pharmacopoeial strength. The commercial chloroform thus treated usually possesses a density of 1.485 at 25°/25°, and a sample examined by the authors conformed with all of the pharmacopoeial tests excepting the sulphuric acid test, thus indicating that it had been purified by washing with water alone.

B. Various other methods have been proposed for the purification of chloroform, especially when it has become contaminated with decomposition products. We have, for example, the method of Gibbs, wherein lead dioxide is employed;[1] that of Mentin, according to which the chloroform is distilled over 2 per cent. of paraffin at 61°;[2] and the recommendation of Shuttleworth[3] that agitation with a dilute solution of sodium thiosulphate be employed.[4]

Yvon[5] stated that he was enabled to obtain an absolutely pure chloroform by treatment with an alkaline potassium permanganate solution; this procedure is not a necessary one, however, and, as a result, has not come into use. Useless also, providing the chloroform has been brought to the proper state of purity prior to fractionation, is the French practice of distilling over poppy oil.[6]

C. Among the *special, technical methods of purification*, the process of Pictet, previously referred to in brief, depends upon cooling commercial chloroform to —80°; the solid bodies are removed by filtration. It is then cooled to below —80° and the non-crystallizable portions, which contain impurities, are removed; the chloroform is then distilled at a very low temperature and the middle 80 per cent. of the product is taken as "chemically pure" chloroform.[7]

[1] Christison (*Pharm. J.*, **10,** 253) found that chloroform keeps well after being once treated with sulphuric acid, but that the continued action of that liquid, especially if it is contaminated with nitrous acid, exerts a decomposing action on it. Tilden (*Ibid.*, [3] **1,** 623) stated that the sulphuric acid used to purify chloroform must be free from all traces of nitrogen oxides, and it was his opinion that the decomposition of chloroform may be attributed to contamination of this kind. Redwood (*Ibid.*, [3] **12,** 734) was inclined to ascribe the improved quality of the British chloroform of 1882 to the care used in its manufacture, particularly to the attention paid to the purity of the sulphuric acid used in the purification. Clark, however, maintained that the presence of nitrous or nitric acids in the sulphuric acid was not the cause of the instability of chloroform. Both Clark and Dott considered "that the decomposition of chloroform is not probably due to the presence of nitric acid in the sulphuric acid" (*vide* Preston, *Ibid.*, **12,** 981). For a discussion of the action of sulphuric acid on chloroform, see *Decomposition*.

[2] Shuttleworth (*Am. Chemist*, **4,** 339) observed that in samples of chloroform imperfectly rectified, as that of the ordinary German manufacture of 1873, the impurities produced by the agencies of time, light, moisture, and atmospheric exposure are, after a lapse of some months, easily recognizable. Traces of sulphuric acid were found to quickly induce this change; and when that chemical has been employed as the purifying agent, and has not been completely removed by repeated washings and rectifications, the product will very soon give sharp indications of decomposition. The method of purification adopted by the British Pharmacopoeia of that time consisted in mixing the chloroform, after treatment with acid, with lime and calcium chloride, and then rectifying at once. Shuttleworth considered that the keeping qualities of the product would be much improved by agitating the chloroform, before rectification, with a solution of sodium carbonate, followed by water. Thorpe (*J. Chem. Soc.*, **37,** 196) purified chloroform by frequently agitating some purest commercial chloroform during several days with successive quantities of water, digesting the decanted fiquid about a week with concentrated sulphuric acid, shaking the separated chloroform with recently heated potassium carbonate, and finally distilling. Chloroform thus purified possessed a density of 1.52637 at 0°/4° and a boiling point of 61.2°. Werner (*Arch. Pharm.*, [3] **25,** 1113) stated that his method of purification afforded a product found to be perfectly satisfactory for medicinal use during 10 years' experience. This method (*Ibid.*, [3] **12,** 481) consisted in shaking the chloroform up with one-fourth its volume of distilled water, removing the latter the next day, then agitating the chloroform with fused sodium carbonate and allowing the mixture to stand 24 hours. After removing the sodium carbonate, the residual product was distilled over a water-bath, the distillate coming over below 64° being used.

[3] Thayer (*J. Phys. Chem.*, **3,** 36) found that traces of alcohol remained in chloroform even after the latter had been allowed to stand over calcium chloride for a long time. He purified chloroform by washing it repeatedly with water, then keeping it in contact with calcium chloride for two days, and finally decanting and distilling over fresh calcium chloride.

[1] See Werner, *loc. cit.*; Thorpe, *loc. cit*; Remys, *Archiv. Pharm.*, [3] **5,** 31; Michaelis and Mayer, *Polyt. J.*, **261,** 496.

[1] *Trans. N. Y. Acad. Med.*, **1,** 146. Gibbs suggested, in 1850, that chloroform possessing an acid reaction and probably containing chlorinated oils be treated with lead dioxide. Metcalfe (*Ibid.*) found that such treatment served to remove any disagreeable odor characteristic of such chloroform.

[2] *Ann. chim. farm.*, [4] **10,** 32.

[3] *Am. Chemist*, **4,** 339. Shuttleworth recommended that chloroform which has been injured by time exposure be restored by agitating well with a dilute solution of sodium thiosulphate, separating from the supernatant liquid and washing with water, then separating and passing the chloroform through filter paper to free it from traces of moisture.

[4] Although this method yielded an improved chloroform, Shuttleworth considered that when a "pure" preparation is desired, the impurities not removable by thiosulphate, those of a more stable character and possessing a higher boiling point than chloroform, be removed by distillation or by treatment with sulphuric acid.

[5] *Mon. Sci.*, March, **1884,** 262. Yvon found that chloroform prepared according to the French Pharmacopoeia of 1866, by agitation with water, leaving in contact with potassium carbonate, drying over calcium chloride, and finally rectifying, is sufficiently pure for anaesthetic purposes. He pointed out, however, that a still purer product could be obtained by modifications of this method.

[6] The method official in the French Pharmacopoeia of 1899 for the purification of commercial chloroform was modified by Masson (*J. Pharm. Chim.*, **9,** 568), according to whose process crude commercial chloroform is first washed with water, the aqueous layer separated, and the chloroform shaken with 2.5 per cent. of its weight of sulphuric acid, and the operation being repeated with a fresh portion of acid, if necessary, the acid being left in contact with the chloroform for two or three days. The chloroform is then treated with 3 per cent. of its weight of sodium hydroxide solution (sp. gr. 1.33), which is left in contact also for two or three days. It is then washed with water, dried over calcium chloride, and 2.5 per cent. of poppy oil added. Distillation is then conducted into graduated receivers containing 0.2 per cent. by weight of alcohol for the amount of chloroform they are to contain. The important modifications in this process are the prolonged contact of the chloroform with the sodium hydroxide solution; the final distillation over poppy oil (it was then employed in the official process for a preliminary distillation); and the presence of a trace of alcohol in the receiver.

The "Chloroforme Officinal" of the present *Codex* (**1908,** p. 148) is prepared from rectified commercial chloroform by agitating with distilled water, decanting and filtering; shaking with sulphuric acid, then allowing to stand over sodium hydroxide; drying over calcium chloride, and finally distilling over poppy oil and adding alcohol (5/1000th part by weight of absolute ethyl alcohol

See also, Maillard and Rane, *Compt. rend. soc. biol.*, **61,** 483.

[7] French Patent 215,911, 1891; U. S. Patent 489,592, 1893. See also, *J. Soc. Chem. Ind.*, **18,** 231. "On Some Peculiar Phenomena in the Solidification of Chloroform," see Pictet, *Compt. rend.*, **114,** 1245.

According to English Patent 15,514, 1891, the purification of chloroform is effected in a copper cylinder, surrounded by a jacket hermetically sealed at the top and bottom, and provided with an inlet and outlet pipe. A grating is fixed at the bottom of the cylinder on which any suitable filtering material can be placed, while a cock is attached below the grating for running off the contents of the cylinder. The object of the purification

On its introduction, it was announced that "Chloroform Pictet" had been experimentally proved to possess a capability of resisting the influence of sunlight for four days. Schacht and Biltz[1] therefore inferred that it contained alcohol, and their prediction that such was the case, without even having seen a sample, ultimately proved to be the case. Moreover, Schacht[2] found that "Chloroform Pictet" suffers the usual decomposition on washing to remove alcohol; and Biltz[3] regarded the decomposition of chloroform under the influence of light and air as a natural characteristic of chloroform and not as a result of impurities.[4] However, DuBois-Reymond[5] stated that "Chloroform Pictet" is affected less by sunlight than any other chloroform with even the addition of alcohol.[6]

J. F. MacFarlane & Co.,[7] separated the following relative quantities of "impurity" from "Chloroform Pictet" and a British product:

	Per cent.
From domestic product	0.0000512
From domestic product	0.0002050
From "Chloroform Pictet"	0.0008200
From "Chloroform Pictet"	0.0004100

Helbing and Passmore[8] examined a large number of samples of chloroform which had been purified by Pictet's process, none of which, however, was anaesthetic chloroform—that is, all the samples were apparently alcohol-free. They found an average specific gravity of 1.5002 at 15°/4° in six specimens, a boiling point of 61.0 61.1° at 756 mm.; and the usual tests with potassium dichromate and sulphuric acid, silver nitrate, and zinc iodide and starch gave negative results. The fractions obtained by distillation were examined and the specific gravity of each determined; in no case was any variation found beyond the limits of experimental error and the temperature rose in no case above 61.1°. In only one case did the residue amount to 0.00005 per cent., or 1 part in 2,000,000, and even then no bad odor was apparent.

The "Chloroform Pictet" examined by the authors possessed a density of 1.491 at 15°/15°, and all the tests for the presence of allowable impurities and decomposition products gave negative results. Four other German products and one American anaesthetic chloroform, all of which were purified by *chemical* treatment, were found to be fully as pure, however, which supports the contention of the authors that purification by cryogenic means is not necessary to secure chloroform of anaesthetic grade.

DuBois-Reymond[1] has studied the physiological action of "Chloroform Pictet" and of the residue of foreign substances obtained in the process of Pictet. He found that the shape of the pulse waves and the frequency of respiration are about equally affected by both substances, the rate of respiration varying freely; that the pulse rate, compared in nineteen cases, is higher at the close of the experiments with the residue than with those with the purified chloroform; that the blood pressure in by far the greater number of experiments at the moment respiration ceases is higher after inhalation of the purified chloroform than after the inhalation of the impure residue; and, finally, that the residue causes stoppage of respiration much more quickly than does purified chloroform. DuBois-Reymond hardly conducted a sufficient number of physiological experiments to enable one to form a definite opinion of the physiological action of the commonly occurring impurities of commercial chloroform which are separated by means of the process of Pictet. In addition, the variable nature of these impurities, owing to the various processes of manufacture and the variability of the crude materials used therein, renders such an investigation of little value unless these facts were considered. This does not appear to have been the case.

(*To be continued.*)

[1] *Brit. Med. J.*, **1892**, i, 209.

is to remove the various substances with which chloroform is invariably contaminated, from whatever source it is prepared, and is conducted in three stages: First, the chloroform in the cylinder is cooled down to —80° by allowing ethyl chloride, ethylene, "Pictet's liquid," etc., to evaporate in the jacketed space outside of the cylinder, and filtering the cold liquid mass; foreign bodies crystallizing above this temperature are thus removed, from which the liquid chloroform is filtered off through the above-mentioned grating. The second stage is to solidify the chloroform thus obtained by reducing the temperature of the cylinder to —82°, when about two-thirds of it freezes against the sides of the container; the remaining liquid is drained off and the solid chloroform is melted (according to Berthelot, chloroform melts at —70°; Haase found the melting point to be —62°; while Archibald and McIntosh reported —63.2°) and run out of the cylinder for the second time. The product thus obtained is finally subjected to distillation at a very low temperature under reduced pressure, the cylinder used in the previous stages of the purification now serving as the receiver; the first and last portions of the distillate are rejected, while the intermediate product, amounting to about 80 per cent. of the total, is obtained as "chemically pure chloroform."

[1] *J. Soc. Chem. Ind.*, **12**, 543. See also, *Western Drug.*, **1891**, 379.

[2] *Pharm. J.*, [3] **22**, 691.

[3] *Ibid.*

[4] See also, Biltz, *Ber. Pharm. Ges.*, **2**, 76, 247; Schacht, *Ibid.*, **2**, 69; Thilo, *Pharm. Ztg.*, **39**, 543.

[5] *Pharm. Centralh.*, **32**, 658

[6] It will be shown under *decomposition* that the changes which occur in chloroform on exposure to air and light are accelerated by the presence of certain impurities. Had DuBois-Reymond made his comparisons of "Chloroform Pictet" with properly purified samples of anaesthetic chloroform, no such differences as he reported could have been observed.

[7] *Brit. Med. J.*, **1892**, i, 525.

[8] *Helbing's Pharm. Record*, March, 1892.

LABORATORY AND PLANT

A MODIFIED WILEY EXTRACTION APPARATUS.

By W. D. Richardson and E. F. Scherubel.

Received November 13, 1911.

Of the making of extraction apparatus there is no end. In almost every laboratory special devices are in use, which have their advantages and disadvantages and their special applications, and each year witnesses the production of new forms or combinations. Of all forms of extraction apparatus, the Wiley apparatus[1] is probably the simplest and

[1] *J. Anal. Appl. Chem.*, **7**, 65; *J. Am. Chem. Soc.*, **1893**; Wiley, "Principles and Practice of Agricultural Analysis," Vol. III, pp. 48–52.

Fig. 1.—Percolating type.

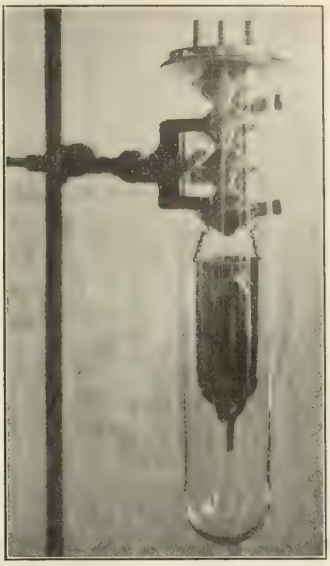


Fig. 2.—Siphon test.

Fig. 3.—Siphon type, inner parts.

most compact. The disadvantages of the original apparatus are the small size of the crucible employed and the difficulty of percolation through an asbestos pad. For many years an apparatus has been in use in this laboratory modeled after the original Wiley apparatus, but modified so as to adapt it to more general use. In Fig. 1 is shown the percolating form of the apparatus. The glass tube is of Jena glass 2 in. inside diameter and 11 in. high; the upper surface of the flange is ground to a plane surface; the cup is of aluminum, 3 1/2 in. high and 1 1/2 in. in diameter; the bottom is perforated with 3/16-in. holes. This cup takes the S. & S. extraction shell 33 × 80 mm. No inner cup is used for weighing purposes, as this would complicate the apparatus. The condenser is 4 in. long. The percolating form of extractor can be used for all extractions to which percolation is ordinarily applied.

Fig. 2 shows the siphon type of extractor, and Fig. 3 shows the inner parts of the siphon type. The siphon cup is 1 1/2 in. in diameter and 3 1/2 in. deep. It is made of nickel-plated brass and has the ordinary siphon tube attached. The inner diameter of the siphon tube is 1/8 in., as larger tubes do not siphon satisfactorily. In using the siphon apparatus it is best to trim off a little of the upper edge of the extraction shell in order to cause it to set deeper into the cup.

This apparatus is, in the writers' opinion, by far the simplest and most adaptable of all forms of extraction apparatus. There are no joints and no opportunities for breakage. The extracted residue is, of course, weighed outside the extraction apparatus in a tared beaker or flask.

One or the other form of this apparatus has been used for the extraction of tankage, cotton seed meats and meals, meat and sausages, soap, etc., etc., and has been found very satisfactory in all cases.

The apparatus is made by E. H. Sargent and Co., Chicago.

LABORATORY OF SWIFT & COMPANY,
CHICAGO.

A SUBSTITUTE FOR THE BLAST LAMP.

By W. A. ERNST.

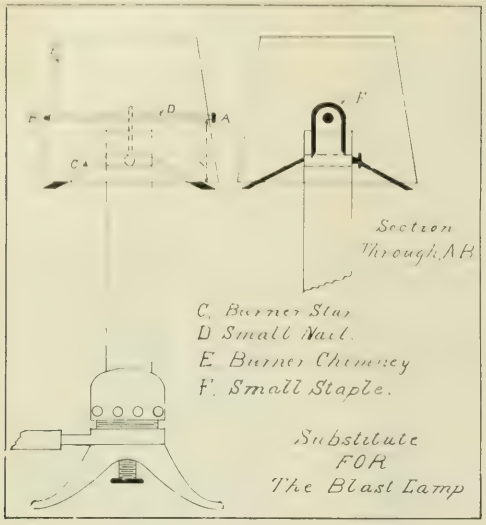
Received November 8, 1911.

The chemist is often required to have a flame which is hotter than the flame from an ordinary Bunsen burner. He can, of course, resort to the blast lamp, but blast lamps, where compressed air is available, are not met with, in most laboratories, and the chemist is obliged to make use of the foot bellows, which, it is well-known, is inconvenient and cumbersome.

The writer, on looking around for some method by which a hotter flame could be produced by the ordinary Bunsen burner, discovered that by making a simple little change in the chimney for a Bunsen burner, an intensely hot flame, almost equal to the blast lamp, could be produced. This flame will be found sufficient for all ordinary purposes, such as making fusions, ignitions, etc.

The accompanying diagram is self-explanatory. A small wire nail is inserted about one inch above the bottom of the burner chimney, and a small wire or staple hung over the nail; this is allowed to go part way into the burner. The height which the nail and staple must be from the burner, must be found for each individual lamp, but can be regulated by moving the chimney up or down by the aid of the burner star. When once the proper height is obtained, all that is

necessary to convert the Bunsen into a blast lamp is to turn on the full force of the gas. An ordinary



flame can be maintained with the chimney in position, by simply reducing the flow of gas.

The best results will be obtained if the nail and staple are kept well within the inner cone of the flame.

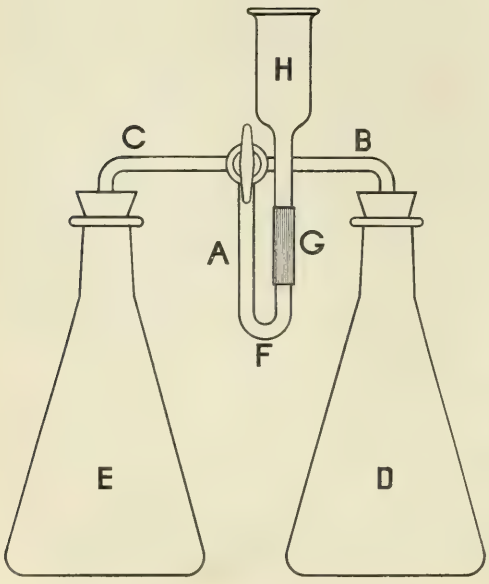
LABORATORY ATLANTIC & GULF PORTLAND CEMENT CO.,
RAGLAND, ALABAMA.

A CONVENIENT FILTERING APPARATUS.

By C. S. WILLIAMS, JR.

Received Oct. 28, 1911.

The accompanying diagram shows an apparatus for filtering by suction, by which portions of the filtrate or washings may be kept separate. The apparatus is especially serviceable when a large number of filtrations are to be made, as in the determination of potash in which it is desirable to keep the excess of platinum chloride solution and alcohol for recovery separate from the ammonium chloride washings.



It consists of a three-way stopcock, a carbon filter, and suction flasks connected as shown. The arm A, at a distance of 6 cm. from the cock, is bent to form the "U," F so that it would extend upward and rest in the joint of the cock. The free end of this arm, A, is cut off about 2 cm. above the "U," giving sufficient length to make the connection to the filter H with the rubber connection G. The filter H may be made secure by binding to the cock with a small copper wire. The arms B and C are bent parallel to the arm A 3 or 4 cm. from their ends, these ends then being passed through rubber stoppers which fit the suction flasks D and E. The suction flasks are connected to the same pump by means of a "Y." By adjusting the three-holed stopper of the stopcock the filtrate or washings may be directed into either or both flasks as desired.

CHEMICAL LABORATORY,
ALABAMA POLYTECHNIC INSTITUTE,
AUBURN, ALA.

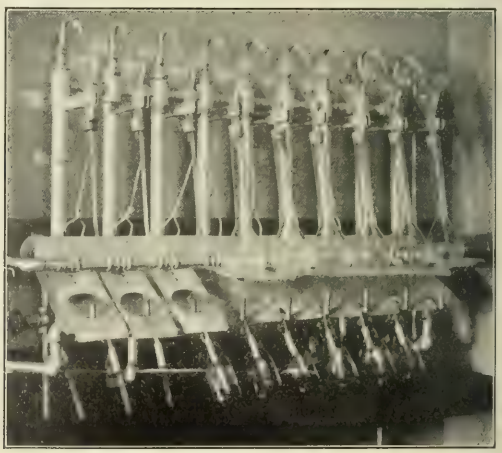
AN IMPROVEMENT ON THE KJELDAHL DISTILLING APPARATUS.

By W. L. HADLOCK.

Received Nov. 6, 1911.

The improvement is essentially a movable support for the flasks.

As shown in the cut, the flask rests upon a sheet of galvanized iron, in one end of which is a hole to re-



ceive the flask. This sheet is attached, by means of two stove bolts, to a framework of heavy galvanized iron wire (No. 4, B. & S. gauge). The framework makes one turn around a three-quarter inch pipe and

then turns upward to form a lever arm. Fastened to the condenser tube about midway is a small wire hook which engages the lever arm when the support is up.

The safety bulb and thistle tube are held rigid by means of an iron band which is fastened around the condenser tube.

The advantages of the apparatus described are as follows:

(1) The block-tin tube cannot be bent in removing the flasks, for the flasks are removed by lowering the supports.

(2) The flasks cannot be bumped off the supports, for the tension of the wire framework holds the flasks tight against the stoppers.

(3) The flasks are easily removed.

(4) There is little danger of losing a determination through leakage at the stopper, for any tendency on the part of the stopper to come loose is overcome by the constant pressure of the flask against the stopper.

(5) All operations are carried on in front of the apparatus.

(6) The apparatus can be fastened to the wall and is thus out of the way.

(7) The different parts are held rigidly in place, and this adds to the appearance of the apparatus.

CHEMICAL LABORATORIES,
WASHINGTON STATE EXPERIMENT STATION,
PULLMAN, WASH

COMMITTEE REPORTS

COMMITTEE ON FERTILIZER LEGISLATION. FERTILIZER DIVISION.[1]

To the Executive Committee and Members of the Division of Fertilizer Chemists:

Your committee has not been very active during the past year and can make only a brief report. Ever since fertilizers were first manufactured, fertilizer legislation has received a great deal of attention from our state representatives and, contrary to what might reasonably be expected, is now receiving more attention than ever before. There is hardly a session of our state legislatures where fertilizers are largely used at which there are not one or more fertilizer bills introduced. Some of these measures are impartial and protect both the manufacturer and consumer, but usually they embody principles which are impracticable and if enacted would impose unnecessary burdens upon the manufacturer. There is no doubt that in many cases the authors of these bills have good intentions, but being entirely ignorant of the fertilizer business, the proposed regulations are unreasonable and impossible of fulfilment. It is also not improbable that in some instances the authors wish to have it appear that they are doing a service to their constituency.

As an example of the class of legislation to which I specially refer I will quote briefly from a bill which was introduced into the Georgia legislature at the last session:

"SECTION 1. Be it enacted by the General Assembly of the State of Georgia, and it is hereby enacted by the authority of the same, that all commercial fertilizers containing or which are designed to develop, as plant food, phosphoric acid, potash and nitrogen which are sold or offered for sale in this State, shall, in addition to the present provisions and requirements of the laws of Georgia, have plainly marked or branded upon each sack or package thereof the sources and ingredients from which the available phosphoric acid, potash and nitrogen, respectively, is generated and obtained, and no contract either written or by parole for the purchase and sale of such fertilizers shall be enforceable in any of the courts of the State against the purchaser of such fertilizers in favor of the vendor or his endorsees, transferees, or assigns, unless such fertilizers are marked or branded as herein required.

"SECTION 2. Be it further enacted by the authority aforesaid, that if any commercial fertilizer or fertilizer material sold in this State, shall prove deficient in any of its ingredients as guaranteed or branded on the sack or package containing the same, and if, by reason of such deficiency, the commercial value of such fertilizers shall fall more than one per cent. below the guaranteed total commercial value of such fertilizers or fertilizer materials, then any note or obligation given in payment therefor shall be collectable by law only for one-half of the amount of such note or obligation; provided, further, that any person, firm or corporation who sold any fertilizer or fertilizer materials that shall prove deficient in any of its ingredients as guaranteed and branded on the sacks or packages containing the same so that by reason of such deficiency the commercial value of such fertilizers shall fall more than three per cent. below the guaranteed commercial value of such fertilizer or fertilizer material, shall be guilty of a misdemeanor.

"SECTION 3. Be it further enacted by the authority aforesaid, that any manufacturer, manipulator, dealer or vendor of commercial fertilizers in this State, who published by branding or who permits to be published by branding, upon the sacks or packages of fertilizers a false or incorrect analysis of the components and ingredients thereof, shall be liable in law to any and every purchaser of such falsely and incorrectly branded fertilizer for all expense, loss and damage sustained by such purchaser by reason of the purchase and use of such fertilizer, the amount of damage, loss and expense recoverable, however, in no case to be greater then 25 per cent. of the original purchase price of such fertilizer.

A deficiency of more than three per cent. below the guaranteed analysis of the fertilizer as published and branded on the sacks or packages thereof shall be

[1] Presented at the forty-fifth meeting A. C. S., Washington, December, 1911.

held and declared by the courts of the State to constitute a false and incorrect publishing and branding within the intent, purpose and meaning of this Act."

It is not necessary to discuss the features of this proposed measure to you who are familiar with the fertilizer business. If we should compile the different laws which have been enacted and the bills which have been proposed in the different states we would not only have an enormous volume, but it would appear that fertilizer manufacturers are about the most unscrupulous class engaged in business. It is of course necessary to have adequate laws to protect consumers and the legitimate manufacturers are heartily in favor of such legislation.

With the years of legislation which have preceded, it would appear necessary only to make some slight modifications from time to time to meet existing conditions, but our representatives seem to have different views.

The main question for this committee to consider is how to meet the conditions as they exist and see that only such laws are enacted as will be impartial and protect both manufacturer and consumer. The question of National legislation has been proposed for the control of interstate business; it is argued that this would serve as a model for the different states. The manufacturers, however, feel that it would have but little influence on the State legislatures and are, as a rule, opposed to National legislation. A committee appointed by the A. O. A. C., who served for several years, compiled the provisions of an admirable law with a view of having a model for the different states, but so far as I know it has not been adopted by a single state.

There is no possible way that I can see of getting a uniform law in all the different states; whatever is accomplished will have to be brought about through the influence of the State Agricultural Departments. These departments are supported by the manufacturing interests, and it should be as much their duty to assist and protect the manufacturer as it is the consumer. The state chemists probably understand the situation better than the other state officials and the manufacturers should have their support and I believe do in most instances, but nevertheless nearly every time the legislature meets it becomes necessary for the manufacturing interests to appear before the legislative committees to enter their protests against unreasonable legislation.

The members of this division should co-operate with the Official Agricultural Chemists for the purpose of obtaining as far as possible some legislative enactments which relate to the analysis and sale of commercial fertilizers.

Another subject which is attracting the attention of fertilizer chemists at the present time and which this division has already had under consideration is the probability of future legislation requiring a statement of Available Ammonia. This would need give us no concern if some chemical method could be devised which would give reliable and concordant results in the hands of different analysts on all classes of ammoniates or even as desirable as the present method for the determination of Available Phosphoric Acid, but the methods now in use, it is generally admitted, do not fully meet the requirements.

Inasmuch as there is still considerable uncertainty about the actual crop value of certain organic materials and the question of analysis presents difficulties which have not yet been overcome, it is to be hoped that our law-makers will not attempt legislation in this direction. With the consumption of fertilizers increasing each year, unless the manufacturers are allowed some latitude in the use of organic materials the farmer will have to pay more dearly per unit for such ammonia as he uses. Chemists have worked out processes whereby many waste nitrogenous materials have been rendered available and we, as fertilizer chemists, should continue this work until there are no waste nitrogenous products not utilized. There are still laws in some of the states prohibiting the use of leather and other similar materials, while it is generally recognized that if properly treated these substances form valuable sources of nitrogen. Instead of prohibiting the use of certain materials, those in authority ought to encourage the working out of methods whereby these materials could be used under certain limitations, if it is necessary to put limitations on ammoniated materials.

I wish to say in conclusion that the writer has, during the past year, had considerable correspondence with reference to fertilizer legislation in some of the Southern States and has personally appeared before legislative committees upon several occasions; the observations and information gained from these sources have formed to a large extent the basis for the comments in this report.

F. B. CARPENTER, *Chairman.*

COMMITTEE ON POTASH. FERTILIZER DIVISION.[1]

The Potash Committee takes pleasure in reporting that the work which has been carried on by them has been recognized by the A. O. A. C. and the modification of the Official Method for Potash determination in mixed fertilizers has been adopted as official, which, according to their constitution, must lay over one year.

The modification is as follows: Weigh 2.5 grams onto 11 cm. filter and wash with small portions of water into 250 cc. flask to about 200 cc. of filtrate; add 2 cc. concentrated hydrochloric, ammonia and ammonium oxalate, cool, make to mark, filter and proceed as usual.

The committee this past six months has analyzed three samples of potash salts by the Official Method for Potash salts and by the Official Method for mixed fertilizer. Some work was done a few years ago by the A. O. A. C. and the referee recommended more work.

In order to establish clearly to our own minds be-

[1] Presented at the forty-fifth meeting A. C. S., Washington, December, 1911.

fore undertaking co-operative work, we worked on samples of Muriate, Sulfate and Kainit.

Our results clearly show that when impurities exist in sulfate there is a decided loss by using the official method for mixed fertilizer, this loss being 0.94 per cent. This sample of sulfate tests 48.12–48.15–48.20 potash by Official Method for Potash salts. On the muriate which tested 52 per cent. there was very little loss. On the kainit scarcely any loss

Mr. Baker, in commenting, says the following:

"The ignitions were made very carefully, and I am certain that the lower results were not due to loss in burning. I note that the sulfate gave a precipitate with ammonia but none with ammonium oxalate. The muriate gave no precipitate with ammonia, but quite heavy precipitate with ammonium oxalate. Kainit—precipitate with ammonia, none with ammonium oxalate.

"The sulfate did not behave properly with the Official Method. There were apparently impurities in the precipitate, and for this reason I believe the lower result to be more accurate.

"I did not note any particular differences in the precipitates of the muriate and kainit. The variation for the muriate is not much, and for the kainit practically none. I may say, however, that in the past I have, upon other samples, obtained much greater differences. I think the indication is that the use of ammonia and ammonium oxalate will produce more accurate results, but in order to draw definite conclusions, it would seem to me that more work should be done along this line."

Mr. Porter remarks:

"I regret that we have not been able to do more work on this subject to report at this time. It has been our experience that some muriates check by the two methods while others show more than two per cent. difference."

The same has been my experience.

In view of these facts it seems to the committee best to recommend further work and an effort be made to have these facts recognized as it is a serious problem for the manufacturer to buy potash on one test and suffer such a loss when tested for in mixed goods.

J. E. BRECKENRIDGE, *Chairman.*

COMMITTEE ON PHOSPHATE ROCK. FERTILIZER DIVISION.[1]

Work is being done on the molybdate method and the acetate method in the sub-committee on iron and alumina. It is proposed, also, to continue work on the determination of moisture and of total phosphoric acid and to describe the procedure for these determinations very carefully. A recent letter from the Bureau of Standards states that on account of press of other work, they have been obliged to postpone further work on the sample of phosphate rock they were analyzing for the committee, but will return to it as soon as possible.

Your committee desires, at this time, merely to report progress and ask to be continued. It has seemed best not to call for co-operative work until improvements in methods now under consideration have been brought into such shape that the committee can confidently recommend them.

ALFRED M. PETER, *Chairman.*

COMMITTEE ON NITROGEN. FERTILIZER DIVISION.[1]

Preliminary results of co-operative work on the analysis of a small sample of commercial nitrate of soda were reported at the summer meeting at Indianapolis, and this report was published in THIS JOURNAL for October, 1911. In the meantime the committee has undertaken the preparation and standardization of a larger sample of commercial nitrate of soda. This sample is now ready to be sent out, and it is expected that the results of co-operative work on this sample will be presented at the coming summer meeting.

PAUL RUDNICK, *Chairman.*

COMMITTEE ON STANDARD SPECIFICATIONS AND METHODS OF ANALYSIS. INDUSTRIAL DIVISION.[1]

The Committee on Standard Specifications submits the following report of its work since the last meeting of the Society in Indianapolis, June, 1911.

At that time a report was submitted covering the progress of the nine sub-committees in charge of the preparation of specifications of the various materials under consideration. The sub-committees on Bleach and Solder had completed their work temporarily and submitted specifications which were embodied in the form recommended by your committee and presented in our report as Provisional Specifications.

The specifications for bleach have not been criticized by the members of the Society during the period since the last meeting and we now believe that they should be submitted to a number of the larger manufacturers for their criticism, after which we would recommend that some action be taken by the Division in regard to them.

The specifications for solder have been criticized and we have referred these criticisms back to the sub-committee.

The sub-committee on Soda Ash have submitted data which will enable us to prepare specifications for the two grades most commonly used.

The sub-committee on Turpentine have considered the subject assigned to them in a most creditable manner and have accumulated considerable data. More or less opposition to specifications was encountered in the case of gum turpentine from the largest producers and sellers, but such a condition is in nowise different from that met with in the case of many other products where the producer does not desire

[1] Presented at the forty-fifth meeting A. C. S., Washington, December, 1911.

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to be hampered by restrictions. In the case of wood spirit of turpentine less objection was encountered but in both cases it was felt that in order to draw stringent specifications it would be necessary to carry on considerable experimental work in order to determine the effect in practice of the variation in gravity, boiling points, etc. It will undoubtedly be possible, however, to prepare a general specification which will enable the consumer to obtain a fair quality of material free from adulteration and escape the gross adulteration which has been practiced in the case of turpentine.

The Committee on Nitric and Mixed Acids has found some inertia on the part of its members, but is of the opinion that specifications for these materials are superfluous and unnecessary. So far as mixed acids are concerned your committee is inclined to agree with its sub-committee, since the strength and quality vary in almost every case where they are employed. In the case of nitric acid, however, we are of the opinion that a general specification should be prepared covering the usual grades for the guidance of those who have only general knowledge regarding the material.

The Committees on Muriatic Acid and Sulphuric Acid have submitted progress reports and it is to be hoped that communications from the other committees will be received in time to present at the Washington meeting.

Your committee feels that it is unwise to submit further specifications at this time, owing to the fact that considerable discussion has arisen as to the proper procedure to be followed in the case of specifications involving methods of analysis. This matter has been made the subject of a communication to the Executive Committee of the Industrial Division, who will undoubtedly outline a definite order of procedure for its committees.

H. J. SKINNER, *Chairman*,
F. G. STANTIAL,
ROBERT JOB.

COMMITTEE ON DEFINITION OF INDUSTRIAL TERMS. INDUSTRIAL DIVISION.[1]

REPORT OF COMMITTEE.

Your Committee on the Definition of Industrial Terms has the honor to report that it has, by correspondence and otherwise, made continued efforts since our last report of a year ago, to determine whether it will be possible to accomplish the objects for which the Committee was formed. In that report it was shown that the efforts of the Committee had met with little support and approval, and in many cases with direct opposition. Since that time there has been no improvement in the situation. The general inertia and decided opposition to the definition of industrial products, especially by manufacturers, has continued. In addition, the requests of the Committee for the expression of individual opinion on this subject and approval of the project have met with no general response.

It seems to the Committee that the difficulty arises from the fact that neither it, the Division of Industrial Chemists and Chemical Engineers, nor the American Chemical Society have any authority to define industrial terms, nor to enforce their use after they are defined. We are in much the same position as if the Society, before the passing of the Pure Food Act by Congress, had attempted to define and enforce definitions of what constitutes pure food. If industrial terms are to be defined, this will have to be done so that definitions can be enforced, or at least accepted. It is suggested that the Bureau of Standards can take this matter up and make recommendations to Congress, but it hardly seems possible that the American Chemical Society can do much in this direction, unless it sees fit to memorialize Congress on the subject.

The Division of Industrial Chemists and Chemical Engineers has a Committee on Standard Specifications, covering materials for which definitions are in almost all cases necessary. It seemed to your Committee on the Definition of Industrial Terms that in drawing specifications for various materials that definition of the material would be necessary. It has, therefore, communicated with the various subcommittees on specifications, with a view of obtaining an expression of opinion from their chairman, as to whether, in preparing their specifications, they would undertake to define industrial terms, and as to whether they thought it practicable to do so. Replies to the inquiries have been received from the chairmen of all the sub-committees, and in general are unfavorable. Under the circumstances, your Committee can do no more than make a statement of the present situation to the Division for its information. It is possible that some lines of less resistance than have been encountered in the past may be developed in the future, and the Committee does not, therefore, ask to be discharged at the present time, unless it is the opinion of the Division that this would be the most satisfactory thing to do. At any rate, the subject should be discussed carefully by the Division, and an expression of opinion given in regard to what is considered the best method of procedure in the future. If no general interest in the matter develops, it would seem that it had better be abandoned.

CLIFFORD RICHARDSON, *Chairman*,
GEO. P. ADAMSON,
J. B. F. HERRESHOFF.

[1] Presented at forty-fifth meeting A. C. S., Washington, December, 1911.

COMMITTEE ON PROFESSIONAL CODE OF ETHICS. INDUSTRIAL DIVISION[1]

Received January 5, 1912.

Your Committee beg to report that after a careful consideration of the subjects, it is their belief

[1] Presented at the forty-fifth Meeting A. C. S., Washington, December, 1911.

that a code of ethics should be formulated and adopted by the American Chemical Society.

There are many instances which can be cited of unethical practices among chemists, such as: misleading advertisements and interviews in papers and magazines; the lending of certificates for advertising uses; the misuse of our science for the purpose of perpetrating frauds on the public, such as the evasion of a standard of purity or the sophistication of a product; slovenly and unreliable work sometimes revealed by impossibly low prices for analytical tests; expert testimony of a character discreditable to the witness and to our profession; a lack of courtesy towards our fellow chemists: and in this respect we stand far below the medical profession.

The present committee of three should be retired, and a larger committee, of perhaps seven members, be appointed, representing the various branches of our profession, and with power to draw up and recommend a code of ethics.

Such work should be done deliberately and with the greatest possible discussion, which can not fail to have a beneficial effect, in pointing out evil practices and elevating our standards of behavior.

This subject has already been discussed at Indianapolis, Louisville and New York, and we believe that each of the several sections would do well to devote one night to the discussion of this problem.

We do not think that for the present, at least, it will be possible or desirable for the American Chemical Society to attempt the enforcement of a code of ethics, still less to examine members with a view to certifying their competency as is done by the Institute of Chemistry of Great Britain; but we do feel that the adoption of a carefully worked out code of ethics, prominently displayed in our publication, would set before us the standard of professional conduct, which, as members of the American Chemical Society, we would be expected to follow, and which would greatly tend to emphasize our brotherly relations to fellow chemists and elevate the ideals of our profession.

(Signed) A. C. LANGMUIR,
C. F. MCKENNA,
L. F. BROWN.

NOTES AND CORRESPONDENCE

A NOTE ON SAMPLING.

By W. J. SHARWOOD.

In the November issue of THIS JOURNAL (3, 861) the Committee on Standard Specifications publishes certain provisional rules for the sampling and analysis of bleaching powder, together with a sliding scale of unit prices founded on the percentage of available chlorine at a base of 35 per cent.

The directions for sampling there given certainly demand criticism and discussion, not necessarily as regards their application to the particular substance for which they were recommended, but because they violate the basic principles of sampling —assuming, of course, that the ideal sample aimed at is a segregated and relatively small portion of material, which shall have a composition exactly corresponding to that of the average mass sampled.

On the other hand, the sliding scale established appears distinctly favorable to the purchaser.

SCALE OF PRICES.

Percentage.	Multiplier for base price per unit.	Relative price per ton.	
31	0.74	22.94	65.5
32	0.82	26.24	75
33	0.89	29.37	83.8
34	0.95	32.30	92.3
35	1.00[1]	35.00	100.0[1]
36	1.04	37.44	107.0
37	1.07	39.59	113.0
38	1.09	41.42	118.0
39	1.10	42.90	122.6

The specific directions for sampling are, in part, as follows: "The sample shall be taken by boring a one-inch hole through the side of the cask, midway from the ends, or through the head near the centre. The sampler, which consists of a stout iron scoop, about three-fourths of an inch wide and eighteen inches long, shall be inserted for two or three inches, withdrawn, and the bleach removed discarded. The sampler shall be inserted again as far as it will go, removed, the bleach transferred to a glass fruit jar, etc."

[1] Base.

Now when material contained in a package varies appreciably in composition from the centre to the surface, the rejection of a portion of the sample, representing a layer of 2 or 3 inches all over the surface, has a vastly greater effect in modifying the average content of the accepted sample remaining than is generally realized. In fact the general adoption of such a system would introduce what is sometimes termed a "little joker," the influence of which may be highly prejudicial to one of the parties to a sale controlled by such a sample. Few seem to realize the fact that a much larger portion of the contents of a package is near the outside than is to be found equally near the centre.

To illustrate the last point it is simplest to consider a concrete example. Let us assume a cask or drum, exactly twenty inches in diameter and thirty inches in length, both internal, the contents of which are to be sampled (Fig. 1). The following table shows, in the last column, the percentage of the total material *remaining*, when a shell of varying thickness, ranging from 0.5 to 3.0 inches, is removed from its entire surface—such a portion as is virtually removed when a similar length is rejected from a scoop or tryer sample.

CALCULATIONS BASED ON A CYLINDER 20 BY 30 INCHES.

Thickness of shell discarded. In.	Diameter of remaining cylinder. In.	Height of remaining cylinder. In.	Area of cross-section. Sq. in.	Approximate volume of remaining cylinder. Cu. in.	Percentage of total volume remaining.
0	20	30	314.1	9423	100.0
0.5	19	29	283.5	8221	87.2
1.0	18	28	254.4	7123	75.6
1.5	17	27	226.0	6100	65.0
2.0	16	26	200.6	5200	55.5
2.5	15	25	176.7	4418	46.9
3.0	14	24	154	3700	39.2

If, therefore, we reject a shell two inches thick, next the surface of the filling of a cylindrical container twenty inches in

diameter and thirty inches high, the portion considered is only 55.5 per cent. of the total. In the case of a smaller container the rejection of a shell of this thickness will, of course, leave a still smaller percentage—with a cylinder sixteen inches diameter, by twenty inches high, only 47 per cent. would remain.

In either case, if deterioration, say to the extent of 5 per cent. of some constituent without change of weight, has taken place in the outer two inch shell, the interior of the package remaining intact, then a sample taken with a tryer as directed will indicate a percentage about 2.5 per cent. higher than the true average content of the package when sampled.

In the case of a material suffering change from decomposition, oxidation, or the loss of a valuable constituent, the purchaser will, of course, suffer by the adoption of such a procedure; in other cases, such as the sale of concentrates or precipitates of high value, shipped in a moist condition, the outside portion becomes enriched by loss of water—such material is, however, almost invariably dumped and mixed before sampling, whether the tryer method or quartering or a mechanical method is resorted to.

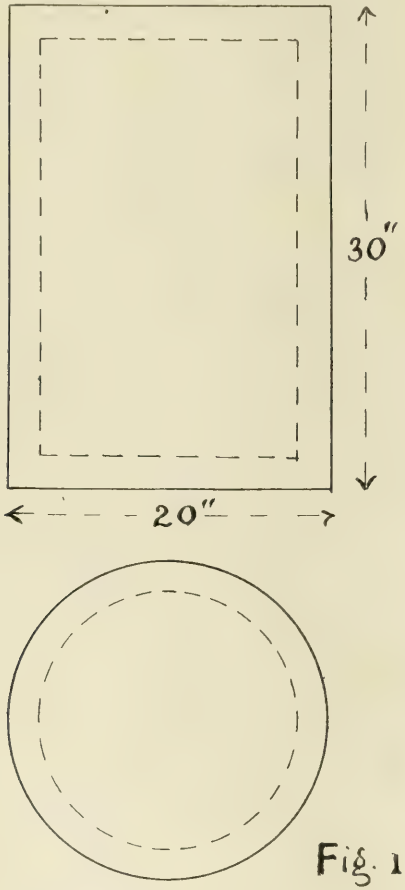

Fig. 1

Similarly, a package of the form of a cement sack, considered as an ellipsoid 10 × 10 × 20 inches, would lose over 51 per cent. by the rejection of one inch over its entire surface, and 86 per cent. by the rejection of a two-inch layer.

Another case may be considered. Suppose the material in a package to deteriorate uniformly from centre to surface. If this is in a cylindrical container, or in a sack, any sample taken with a cylindrical tryer, reaching to or past its centre, will show a percentage better than the true average, no matter in what direction the tryer is thrust. This form of tryer tends to take, in the case of such a substance as bleach, a sample of too high a percentage, even if the surface layer is not discarded.

This, also, is perhaps best shown by a concrete example: Assume a cylinder as before, twenty inches in diameter, and for simplicity's sake assume that no change of weight occurs and that no deterioration takes place at the ends of the cylinder, but only from the axis outward. Let the central portion of the mass retain its original percentage of a certain constituent, say 36 per cent., which at the circumference is diminished to 31 per cent. This is indicated in the sectional diagram (Fig. 2) and it is obvious that at two-inch intervals indicated

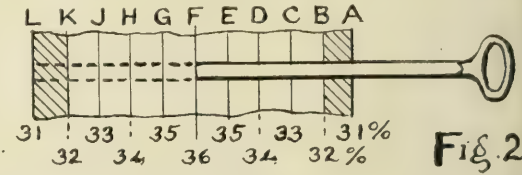

Fig. 2

by B, C, D, etc., the percentages will be 32, 33, 34, etc., as there shown. The true mean percentage over any normal cross-section will be $31 + 36 - 31/3 = 32.67$ per cent.

The following table shows the percentage actually contained in a sample taken with a cylindrical core tryer reaching to the centre (F) and to various distances beyond it, and also the additional effect of discarding the outermost two inches from the sample.

PERCENTAGES SHOWN BY CORE SAMPLE (SEE FIG. 2)—ACTUAL PERCENTAGE OF GIVEN CONSTITUENT, 32.67 PER CENT.

I. Preserving entire sample.		II. Rejecting outer 2 inches.	
Portion sampled.	Percentage of constituent in sample.	Portion sampled.	Percentage of constituent in sample.
AF	33.5	BF	34.0
AG	33.83	BG	34.3
AH	33.93	BH	34.33
AJ	33.75	BJ	34.2
AK	33.72	BK	34.0
AL	33.5	BL	33.72

In general, therefore, the method prescribed by the committee would yield a sample containing 34 per cent. or a little more, instead of the actual average of 32.67, while an unmodified tryer sample would show a little under 34 per cent.

But this is not all. Under the sliding scale recommended for bleaching-powder the unit price increases as the percentage increases, and the price per ton goes up in a duplicate ratio.

		Relative cost per gross ton.
True content.....	32.67% at 0.89 × base = 29.076	90
Content of tryer sample.	34% at 0.95 × base = 32.30	100

In such a case, therefore, the use of the tryer method of sampling will make the cost to the purchaser about 10 per cent. higher than he would pay on the basis of the actual content.

In the case of the contents of a round (approximately spherical) package, the centre of which differs appreciably from the outside, the only truly representative sample possible would be one of conical or pyramidal form—the apex at the centre of the mass. As a matter of fact it is perhaps fortunate that the sample drawn with a straight scoop tryer often actually gives some sort of approximation to a conical form, for there is a greater tendency to lose material from the interior than from the exterior portion of the mass sampled, if the latter is

not deliberately rejected. When such packages are sampled a tryer tapering toward the tip ought to be preferred, if an ideal sample is aimed at. Under the circumstances indicated, when

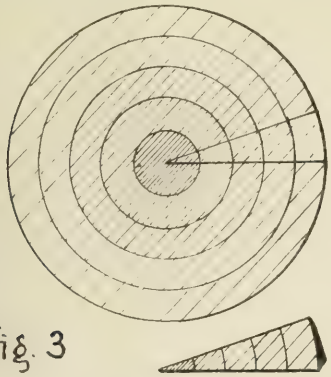

Fig. 3

a cylindrical core is taken, the sample will only be accurate if a sufficient number of cores are drawn in various directions and equably distributed.

LEAD, S. DAKOTA,
December 4, 1911.

LABORATORY PREPARATION OF LITMUS PAPER.

Experience has shown that with a good quality of litmus paper, uneducated workmen are able to distinguish slight differences in shade, and maintain very slight acidities or alkalinities, if such are desired. It is found, however, that they are often deceived by the quality of the litmus paper, which, through varying amounts of salts in the paper, may require widely differing amounts of acid or alkali to give a definite color.

Practically all directions for the laboratory preparation of litmus paper start with commercial litmus and require from 10 per cent. to 33 per cent. solutions to make a sufficiently colored paper. Various methods of purifying this commercial product before its use may be found in the literature, all of which require considerable time for sedimentation, and, usually, quite an amount of alcohol, which makes purification expensive. A great many have used a water extract of commercial litmus without further purification, neutralizing to meet their requirements. This gives a paper which is satisfactory for some purposes, but the red paper is usually rather impervious to water, and the large amounts of soluble salts which it contains cause reactions in the paper which are often deceiving.

These various difficulties have led to the use of the chemically pure litmus which is sold by the various supply houses and can be prepared in about one-quarter of the time required by the ordinary substance. Although the chemically pure litmus is listed at ten times the value of the commercial product, its coloring strength is so much greater that the final cost is never more, and in some cases is less. Continued trials have shown the following to be a very satisfactory grade of litmus paper for all purposes, whether laboratory or manufacturing, and the product will be found more delicate than most litmus papers on the market.

For blue paper, 1.4 per cent. of chemically pure litmus is dissolved in distilled water with constant shaking for about one hour. This solution is set aside over night, carefully decanted from the small amount of sediment, and sulfuric acid added, drop by drop, sufficient to reduce alkalinity to such a point that a piece of filter paper floated on the top and then dried will assume a very perceptible red color after being suspended one-half minute in $N/2000$ hydrochloric acid.

To make red litmus paper a 1.0 per cent. solution of chemically pure litmus is required with the addition of sulfuric acid until such a degree of acidity is reached that a very perceptible reaction will take place when paper floated and dried as before is suspended one-half minute in $N/4000$ caustic soda solution.

Time of exposure to these standardizing solutions is found to be as important a function as the degree of acidity or alkalinity of the paper. The above-mentioned degrees of sensitiveness are close to the practical limits, for if the papers are made more delicate they cease to be red and blue, but become lilac or neutral.

The filter paper used is any smooth compact qualitative paper sold by the chemical supply houses. The best manner to saturate the paper with litmus has been found to cut it in strips about seven inches wide and to draw the paper over the surface of the litmus solution, which has previously been placed in an ordinary shallow square-cornered enameled bread-baking pan. The paper is held by the ends and first touched to the surface of the liquid, about two inches from one end; then the other end is released and the paper drawn down across the edge of the pan. Surface tension holds the paper to the liquid, yet only one side of the paper is allowed to touch the solution, and drawing across the side of the pan takes away any excess. The strips are hung up to dry by pinning the blank ends over lines stretched in some convenient place.

The paper will be found very uniform, as just sufficient solution will have been taken up to dye all the sheets of the same shade. One liter of solution will make one hundred sheets seven inches by twenty inches in size.

These sheets may be rolled up or packed away in proper containers to protect them from the air, and cut in strips of convenient size for use shortly before they are needed. Wide-mouthed, glass-stoppered bottles are found very convenient for holding the small strips for daily use. Great uniformity is secured by making up large batches at a time, and the method allows for closest similarity of succeeding batches.

E. W. RICE.

PERILLA OIL.

Product from the seed of *Perilla ocimoides* (Nat. Ord. Labiateae), an indigenous plant of India, China and Japan. Perilla oil is very similar to that of linseed. In Manchuria, it is used for edible purposes. The Japanese use the oil for waterproofing paper umbrellas, and for preparing transparent paper for windows.

In the colder portions of Japan, the plant is grown as a field crop. The annual production of seed is about 300,000 bushels. A bushel of seed gives up a gallon of oil, worth 70 cents per gallon.

U. S. Consul Sammon, Yokohama, Japan, in 1910 suggested the introduction of this plant into the United States. Following this suggestion, a small quantity of the seed was imported from Japan. During the season of 1911, this plant was grown at Akron, Ohio. Seed were sown April 15th; plants came up 10 days later; growth slow; bloomed Aug. 25 to Sept. 1st; harvested Oct. 1st, after plants had been injured by frost. Plant resists light frosts, but cannot resist drought.

On the dry, sandy soil of West Akron, the plant did not do well. On the damp, clayey soil the growth was much better.

Yield of seed based on very small area is about 400 pounds per acre. The seed of this Ohio-grown perilla was 20 per cent. lighter, per equal volume of seed than the parent seed. The crop did not fill well; about 80 per cent. of the seed pockets

contained well formed seed. Many of the seeds were of light weight. Japanese perilla seed contains, according to Lewkowitsch, 38 per cent. of oil. Our sample of imported seed gave by benzole extraction, 45 per cent. The Ohio grown seed contained 41 per cent. oil. Domestic perilla oil was thinner than the foreign oil. The oil extracted from Japan grown seed gave a distinct linseed oil odor. The odor of Ohio oil was that of the fresh plant—a strong minty odor. These peculiarities were, perhaps, due to fresh seed.

Compared with linseed oil, perilla oil dries slower than linseed, but gives a better film. Perilla oil film is smooth, glossy and tough. The usual objection to perilla oil is the difficulty in spreading, this oil having a tendency to gather in globules. This has not been the case in our experience.

Parallel experiments with linseed oil show that its spreading qualities are equally as good as those of linseed. Tests on paper, imitating Japanese umbrella work, indicate that linseed oil is superior for this work. Old oil or oil that has been heated may give better results.

Compared with flax as a suitable crop for Ohio soils, perilla returns a less oil value per acre, and has no valuable by-products. Perilla press cake is of doubtful value as a cattle food. The green stem may yield an essential oil of value, though the plant is quite dry when the ripening of the seed occurs.

CHAS. P. FOX.

BARLEYS EXHIBITED AT THE SECOND INTERNATIONAL BARLEY AND HOP PRIZE EXHIBIT.

Of the 107 specimens of barley entered 53 were of the Manchuria, 26 of the Bay Brewing and 28 of the two-rowed class, of which latter 7 specimens came from Germany. Of the 1910 crop there were 9 specimens in the *Manchuria* class and 4 in the two-rowed. The 1910 Manchuria class barleys average higher than the 1911. The Wisconsin pedigreed barleys grown from seeds disseminated by the Wisconsin Agricultural Experiment Station took the largest number of prizes. Practically all of the pedigreed samples belonging to the six-rowed variety had a 1000 berry-weight within the permissible limits. Of the 1911 crop five samples were disqualified for demerit, and of the 1910 crop one, in both cases owing to generally poor quality; four of these on jury inspection alone. In the samples of the Manchuria class the albumen content varies between 11.2–15.5 per cent., and the 1000 berry-weight between 24.4 and 32 grams.

The *Bay Brewing* barleys generally have an albumen content below 10 per cent. which is considerably lower than the Manchuria, whose average is approximately 12 per cent. In the samples of the Bay Brewing type, the Nitrogen ranges from 7.3–10.3 per cent., and the 1000 berry-weight between 36.1–47.1 grams, only 50 per cent. of the total number of samples having a berry-weight higher than 42 grams. The vitality or germinating capacity of these Californian barleys is also considerably higher and varies between 100–97 per cent. These Bay Brewing barleys conform in their characteristics more nearly to the *two-rowed* barleys of the far West, like Idaho, Montana, and California. With a few exceptions, the two-rowed barleys of the Middle Western States were disqualified for excessive albumen content, which was 13.5–19.6 per cent. The Nitrogen content in German barleys is 9.1–10 per cent., in American Western two-rowed 7.5 per cent. The superiority of the Western two-rowed barleys over the Eastern is noticeable on almost every count.

From the analytical and jury results it seems evident that the climatic, soil, and other cultural conditions of the barley growing sections of Idaho, Montana and the Coast, are better suited to the growth of barleys that conform to the European type in their brewing qualities, than the barley growing sections east of the Rocky Mountains, which seem to be the home of the Manchuria, Oderbrucker and related varieties. Whether these Manchuria varieties will do as well or better in the Western area, where they have been introduced, for instance in Montana, remains a matter of future concern.

ROBERT WAHL.

EIGHTH INTERNATIONAL CONGRESS NOTES.

Among the features of the Eighth International Congress of Applied Chemistry which are of interest and importance, are the general lectures, presenting a review of some branch of chemical activity by an acknowledged authority. These lectures are only a part of the return that these International Congresses endeavor to make to the country whose hospitality they enjoy. At the Eighth Congress, which meets in New York and Washington, September, 1912, the following lectures are now announced:

"Some Physical Aspects of Molecular Aggregation in Solids." By GEORGE BEILBY, England.

"The Role of Very Small Amounts of Chemical Substances in Biochemistry." By Professor GABRIEL BERTRAND, France.

"Photochemistry of the Future." By Professor G. CIAMICIAN, Italy.

The exact dates for these lectures will be announced later.

OBITUARIES

DR. NAOKICHI MATSUI.[1]

The scientific world sustained a great loss by the death of Dr. Naokichi Matsui, Doctor of Science and Dean of the Agricultural College of the Imperial University of Tokyo, upon the first day of February, 1911.

Dr. Matsui was born at Ogaki, in the province of Mino, in 1855, and studied chemistry at the University of Tokyo. He went to the United States in 1875, as first Japanese Government student, with several other young men, among them Marquis Komura, Dr. Hatoyama, Dr. Hirai and a few other brilliant young students, and devoted himself to the study of chemistry at the School of Mines at Columbia University, under Prof. Chandler and others. He obtained the degree of Bachelor of Philosophy in 1878, from the same university, and was awarded the degree of Doctor of Philosophy in 1880, by presenting a thesis on "Kaolin of Arita." When he returned to Japan in the same year, he was appointed lecturer in the Science College of the University of Tokyo. In the following year he was appointed a professor in the same university, and taught chemistry exclusively in the Science College and Preparatory School.

When the Imperial University was founded in 1886, by amalgamating the University of Tokyo and the College of Engineering, he was appointed a professor of the Engineering College. In 1888 he was awarded the degree of Doctor of Science.

In 1890 he was appointed a professor and Dean of the Agricultural College of the Imperial University of Tokyo, which position he held over twenty years, until his death.

Dr. Matsui went to Europe and the United States in 1900, and returned to Japan after an absence of one year. He succeeded Prof. Yamakawa as President of the Imperial Univer-

[1] Translated from the *Journal of the Tokyo Chemical Society*, April, 1911.

sity of Tokyo in 1905, but resigned after a short period and resumed his former duties.

His Imperial Majesty, the Emperor of Japan, conferred upon him the order of the Sacred Treasure in 1908, for his innumerable services, and when he heard of the declining health of Dr. Matsui in the early part of 1911, the Emperor conferred upon him the order of the Rising Sun.

After his appointment as Dean of the Agricultural College of the Imperial University, Dr. Matsui employed his spare moments toward the development of the University, as councilor of the University, committee on hygiene and councilor and chairman of the committee of the University library. He also did much toward developing the educational system of Japan, as a member of the committee on compilation of English readers, the special committee on investigating the subsidy for industrial education, and the committee on selecting teachers for Normal Schools, Middle Schools and Higher Girls' Schools, etc. His valuable services toward the development of Fine Arts and the improvement of industry in Japan cannot be exaggerated, as he was at one time or another councilor of the Administrative Bureau of the Special Exposition, juror for the Second Exposition of Marine Products, and juror for the Anglo-Japanese Exposition, etc.

Dr. Matsui joined our Tokyo Chemical Society when he returned to Japan in 1880, and was elected President of the Society in the same year. For nine years he served the Society either as Secretary, permanent member, or President. He had very little time for research, as he was busily engaged in the discharge of the duties above mentioned. But he made a report of the notes of his experiments on Kaolin of Arita in 1880, and the result of the experiments regarding the liquid extinguisher in 1885 at the Tokyo Chemical Society. He also lectured on the following subjects:

History of the Atomic Theory (1882).

The Relation between Chemical Construction and Magnetic Polarization (1884).

Traube's Experiment Relative to the Function of Water on Oxidation (1884).

Crookes's Theory of the Atom (1887).
Regarding Nitrification (1892).
Theory of Electrolytic Dissociation (1892).
Chemistry of the Digestion of the Stomach (1894).
Chemistry of the Digestion of the Intestines (1895).
Chemistry of Respiration (1897).
Regarding Fischer's Research on Uric Acid (1900).
Regarding the Composition of Camphor (1906).

Dr. Matsui contributed not a little service toward the development and diffusion of chemistry in our country. We can readily attribute the present prosperity of the Agricultural College to the untiring efforts of Dr. Matsui. His fame in the educational circles of science in our country will never be forgotten.

CONSULAR AND TRADE NOTES

GERMAN BRONZE-POWDER INDUSTRY.

Nuremberg is the center of the bronze-powder industry in Germany. With the exception of one factory at Munich and one at Frankfort-on-the-Main, all bronze-powder factories of any magnitude are located in Nuremberg and Fuerth and the smaller towns in this vicinity.

There are here 15–18 concerns of considerable extent and about 25 smaller factories, which employ an aggregate of 1,200 workmen and turn out an annual product of the value of about $3,000,000. Experienced workmen are paid 9–10 cents per hour and work 10 hours a day, except on Saturdays, when 8 hours is the rule. The few men employed in the foundry departments are slightly better paid—about 12 cents per hour. Juvenile employees average about 7 cents per hour. Practically no female workers are employed. Almost without exception factories are located where cheap water power may be had.

The raw materials used in the manufacture of the better grade of bronze powder are copper and zinc. For cheaper grades various kinds of metal scraps from the toy and other factories are mixed with these two basic metals.

The metals, mixed in graphite crucibles, are reduced to a molten mass and cast into half-round ingots about 12 inches in length and about five-eighths of an inch in thickness. The ingots are flattened under water-power hammers and passed through rollers until they are extended into metal ribbons many yards in length. They are then cut into strips about 2 yards long, tied into bundles of approximately 100 each, and hammered out still thinner. After being subjected to another annealing process two or three of such bundles are tied together and again hammered. At this stage the thin metal sheets are put through a cleaning process, tied into still larger bundles, and again beaten out under hammer. When the required thinness is secured the sheets are cut and torn into shreds and placed in hermetically closed iron boxes, in which they are pounded into a powder under vertical iron stamps. They are passed from one stamp mill to another until reduced to the fine metallic flour known as bronze powder.

Bronze powder is to-day invoiced for export at 20–38 cents per pound, according to quality, the price for a fair-grade product being about 27 cents per pound. Extra fine grades sell as high as $1, and even more, per pound. These figures include packing charges, insurance, and freight to Bremen, which amount to about 60 cents per 100 pounds.

Exports of bronze powder and metal clippings (the raw materials for bronze powder) from Nuremberg to the United States for the last four years were as follows: Bronze powder—1907, 934,732; 1908, $408,140; 1909, $558,336; 1910, $525,168. Metal clippings—1907, $80,585; 1908, $167,401; 1909, $217,781; 1910, $236,799. These figures would indicate a considerable increase in the manufacture of bronze powder in the United States.

ELECTROLYTIC RECOVERY OF ZINC.

Consul-General Thomas Sammons, Yokohama, Japan, reports that a new process for the electrolytic recovery of zinc has been successfully worked out by Mr. Chitaro Yoshida, the proprietor of a copper mine in Iwashiro Province, Japan. The zinc ore is dissolved in the electrolyte, and from this liquid the zinc is precipitated by electrolysis. The process is simple, but several obstacles have been found. For instance, the presence of a small particle of copper, antimony, or arsenic is enough to render the process futile. One of the defects of the process heretofore has been the spongy form of the zinc which adhered to the cathode. To prevent this, carbon was tried instead of lead in the anode. The carbon was coarse and dissolved in the sulphate of zinc, and the zinc which gathered on the cathode was then found to be refined to a degree rarely surpassed by the imported metal.

During 1910 Japan exported 24,747 tons of zinc, valued at $383,485, and imported 11,581 tons. It is believed that a new industry will be built up in Japan as a result of this new process.

SULPHUR MINES IN MEXICO.

Consul Wilbert L. Bonney reports that the great bulk of Mexican sulphur is obtained from the mines near Cerritos, in the State of San Luis Potosi, about 50 miles east of the capital. The deposit is one of the largest and richest in the world.

The production of the mines is about 800 metric tons of refined sulphur per month. The sulphur is encountered at a depth of 20 feet below the surface, and the lowest present workings are 190 feet deep. The mines are at an elevation of about 5,800 feet above sea level. The indications are that the sulphur extends downward indefinitely in chimney form. The ore runs to 37–90 per cent. pure and is smelted by the steaming process.

Of the product about one third finds a market in Mexico, the present price being around $32 per metric ton. The mines employ some 700 men. The property is owned by the Virginia-Carolina Chemical Co., but is under lease to German interests. The excess over home-market demands is shipped to Germany.

There are traces of sulphur in other parts of the State, and sulphur compounds are common among ores. At Venado, about 50 miles north of San Luis Potosi, a sulphur deposit has been uncovered, but its output would be small compared with the Cerritos mines. The Venado deposit lies in a blanket some 10 feet wide practically on the surface, and the product shows about 30 per cent. pure sulphur. The operating company had its ovens installed by an Italian expert after the manner of the Italian smelting practice, but the capacity of the works will not exceed 3 to 4 tons per day under favorable circumstances.

AMALGAMATION OF BRITISH CEMENT COMPANIES.

Consul-General John L. Griffiths reports that a project has been formed to amalgamate a number of British cement works as the British Portland Cement Manufacturers (Ltd.). "It will have an issued capital of $17,032,000, and there will be "no public issue of stocks or shares, and no prospectuses will be circulated."

It is stated that the new company, the formation of which is practically assured, will control an annual output of about 1,500,000 long tons of cement. The company, in addition to purchasing the stock of certain local companies, will have a working agreement with the Associated Cement Co., and the combined capital of this company and of the British Portland Cement Manufacturers (Ltd.) will be about $58,398,000. It is claimed that the two companies will control five-sixths of the cement production in Great Britain.

ARGENTINA'S WINE INDUSTRY.

Vice-Consul General R. J. Hazeltine, Buenos Aires, advises that the importance of the wine-making industry in Argentina is steadily increasing, owing to the efforts of interested capitalists, although this industry may be said to be still in its infancy.

The latest statistics obtainable show that the annual production of Argentine wine amounts to 92,459,662 gallons, the value of which in the warehouses is $25,263,700 United States gold. The 142,500 acres devoted to the vine represent a value of $72,606,600, and the warehouses are worth, in addition, $21,230,000. Thus the industry as a whole represents a value of $119,100,300 United States gold.

Estimating the total population of Argentina at 7,000,000 persons, the production of wine is 13.2 gallons per capita annually. The exports of wine from Argentina are inconsiderable.

PETROLEUM OUTPUT OF THE WORLD.

The total output of crude petroleum in 1910, for the world, was 327,472,256 barrels of 42 gallons each, against 298,326,073 barrels in 1909. Of this amount the United States alone produced 209,556,048 barrels, passing the 200,000,000 mark for the first time. In 1909 its production was 183,170,874 barrels. The Canadian production has been decreasing steadily since 1907, while the imports into that country have been on the increase. Production of oil did not increase greatly in Mexico during 1910, but the results of explorations in that year made large supplies certain and gave to Mexico the competitive position toward the United States that has long been imminent. Mexico's production of crude petroleum rose from 1,000,000 barrels in 1907 to over 3,000,000 in 1910, while the Mexican imports of crude and refined petroleum from the United States increased from 19,207,159 gallons in 1908 to 43,381,272 gallons in 1910.

The production of the leading countries for 1909 and 1910 is given in the following table, in barrels of 42 gallons:

Countries.	1909. Barrels.	1910. Barrels
United States	183,170,874	209,556,048
Russia	65,970,350	70,336,574
Galicia	14,932,709	12,673,688
Dutch East Indies	11,041,852	11,030,620
Roumania	9,327,278	9,722,958
India	6,676,517	6,137,990
Mexico	2,488,742	3,332,807
Japan	1,889,563	1,930,661
Peru	1,316,118	1,330,105
Germany	1,018,837	1,032,522
Canada	420,755	315,895
Italy	42,388	42,388
Other countries	30,000	30,000
Total	298,326,073	327,472,256

OIL FROM SUNFLOWER SEED.

Consul Walter C. Hamm, Hull, England, reports that experiments are now being made at some of the crushing mills in Hull as to the feasibility of extracting oil from sunflower seed and using the residue as an ingredient in the manufacture of feed cake. Large consignments of seed have recently arrived in Hull from Odessa, the sunflower being extensively cultivated in southern Russia.

When crushed the sunflower seed yields on the average 30 per cent. of oil, while the yield of soya-bean oil is 18 per cent. The oil is limpid and pale yellow in color, and it is believed it will prove valuable in soap-making, the manufacture of varnishes, and for culinary purposes. The residue from the crushed sunflower seeds has been manufactured into cakes, and experiments are being made to ascertain whether the cake thus made is suitable for feeding purposes.

Experiments have not gone far enough to give any exact data as to the value of the oil or the meal. No market prices can be stated as there has been no demand, and no trustworthy comparison with other oil and cake producing seeds can be given as yet.

GAS PRODUCTION AND CONSUMPTION IN ENGLAND.

The annual Board of Trade returns show that there are now 298 municipal gas undertakings as compared with 293 a year ago. The private companies have increased in number from 501 to 511. These 809 gas undertakings in 1910 manufactured 198,733,353 thousand cubic feet as against 93,574,394 thousand in the previous year. The revenue form this was $152,205,622, the expenditure being $112,958,176. The municipalities were responsible for the supply to 2,666,146 consumers (compared with 2,590,270 in the preceding year), and the private companies 3,751,703 (in contrast to 3,573,796 in 1909). The companies made a gross profit on working (not allowing for dividends or loan charges) of $25,001,692, the municipalities $14,245,720.

BOOK REVIEWS

Some Chemical Problems of To-day. By ROBERT KENNEDY DUNCAN. 254 pages, 34 Illustrations. New York: Harper & Brothers 1911. Price, $2.00.

The eleven chapters composing this volume deal with many diverse subjects, but always in the breezy style characteristic of the author. The titles range from "The Beginning of Things," or the Chamberlin-Moulton planetesimal hypothesis, to "The Question of the Atom" and its constitution. Some are purely chemical, and one describes the "Relation of the University of Wisconsin to the State." In the latter, the ways in which members of the University assist, officially, as experts, in the scientific drafting of legislative acts, and on the Railroad Commission which controls all the public utilities in the State, are set forth with gusto. The substitution of experts in finance, political science, and engineering, for the usual aggregation of saloon-keepers and men who turn to politics because they cannot make a living in any other line, is certainly an experiment worthy of wide imitation.

The favorite themes of the author are seldom missing. "The Prizes of Chemistry" calls attention to materials, like cobalt, tellurium, silicon, soap-weed fibers, cull oranges and cocoanut husks, which could be obtained in quantities, if only some one would devise extensive uses for them. It summons chemists to the production of untarnishable silver, more resistant enamels, harmless bleaches, soaps with soluble calcium salts, and special glues. The "Trend of Chemical Invention" shows the sorts of things that, judging from the patent records, seem at present to be most needed, and how the patentees think they have supplied the needs. Each subject yields its quota of problems for "research fellows," and the number of new fellowships reported shows that the supply is responding satisfactorily to the demand. The chapter on "Bread" explains how the isolation and commercial production and use of the ferment of salt-rising bread have been brought about by one fellow, and discusses other problems in process of solution.

There is much significance in the conclusions of the paper, "On the Relation between Chemistry and Manufacture in America." An investigation showed that the research chemists in American factories, where they exist, are often badly selected in the first place, are frequently ill-directed—being occasionally even under the works foreman—are under-paid (average pay $60 per month), and are often excluded from schemes of promotion applying to other classes of employees. The remark that the factory is a place where they make things, and that it wants ways of making new alloys, new glasses, and so forth, while the training of the chemist has usually taught him only how to analyze things, is a distinct hit. As the author says, "too often the men appointed to the task are beaten before they begin, by their very habits of thought."

The book contains much that will be interesting and suggestive to the chemist, as well as a fund of information, and some thrills for the "intelligent reader" who is not a chemist. The excellent illustrations will be of especial value to the latter. The author probably would not put the manufacturer in either of these classes, but even the employer would benefit by glancing through its pages. ALEXANDER SMITH.

The Manufacture of Chemical Manures. By J. FRITSCH. Translated from the French by DONALD GRANT with valuable notes by translator. 764 pages. Scott, Greenwood & Son, London. D. Van Nostrand Company, New York. Price, $4.00 net.

This work treats of the subject from the French standpoint and is brought up to the English standpoint by the translator.

While there are many useful suggestions as to the manufacture of fertilizers, the machinery is somewhat different from that used by American manufacturers.

Valuable information is given as to history and origin of phosphoric acid in nature, the principal phosphate deposits, drying and enrichment of phosphates.

Superphosphate manufacture is reviewed from 1850 to 1908 and the theory as well as practice of manufacturing of soluble phosphates is treated at length. Soluble phosphate being that portion soluble in water and not what is termed "available" in America, is soluble in water plus that which is soluble in neutral citrate of ammonia.

Grinding of the rock, acidulating, storing, drying and curing of the superphosphates are considered in detail.

Valuable suggestions as to manufacture of phosphoric acid and double-superphosphate are given also.

Nitrous manures are treated completely, including waste materials, such as leather, hair, wool, etc., cyanamide, nitrate of lime, sulfate of ammonia, nitrate of soda, blood, horn, meat meal, peat and guanos.

Potassic manures are adequately covered, including the Stassfurt salts as well as the manufacture of potash salts from feldspar and other potassic minerals.

Basic slag as to its origin and nature is considered. The chapter on the transference and handling of raw materials and finished products is very interesting and valuable reading.

There are many valuable tables of analysis, including those of phosphate rock, potash salts and nitrogenous manures.

The book as a whole is a valuable contribution to the subject of commercial fertilizers. J. E. BRECKENRIDGE.

The Technical Analysis of Brass and the Non-ferrous Alloys. WM. B. PRICE AND R. K. MEADE. 267 pp. 12mo. John Wiley & Sons, New York. Price, $2.00.

The book is divided into three parts: the first gives a general description of the commercial non-ferrous alloys, the second gives general methods for the determination of the principal metals, silica, sulphur and phosphorus, and the third part is special methods for particular alloys.

The first part covers the subject as well as it can be done in the very limited space. The tables of analyses give typical examples but, unfortunately, the authors do not state that these analyses are merely typical and it is liable to confuse the reader when he finds two entirely different analyses of, for instance, Delta metal. It should have been clearly stated that each maker has his own formula for each alloy and that there is often considerable variation in the composition of any when made at different times by the same concern. No methods of physical testing are included, which is unfortunate as they are often of more importance than the analyses.

The second chapter of the introduction gives a description of the apparatus used in electrolytic analysis. The types described are good, the descriptions are clear and they are well illustrated by simple line drawings.

The second part takes up the elements commonly found in commercial alloys and, as a rule, gives gravimetric, volumetric and electrolytic methods for each. The descriptions are very complete except in one particular. The expression "strong acid" is used continually without any statement of what strength is meant by it. Strong is a purely relative term that is used with very different meanings. Most of the methods

given are good. The authors do not mention the fact that precipitates of the hydroxides, especially if precipitated by ammonia, are almost certain to contain silica, and often phosphoric acid, in sufficient quantity to cause serious error. Under lead they advise washing the precipitate of sulfate with a mixture of water, sulfuric acid and alcohol; this is apt to give high results as very few sul ates are readily soluble in alcohol. The precipitate should first be washed free from sulfates with dilute sulfuric acid and, after this has drained off, with alcohol. For the volumetric determination of manganese they give the old Williams method apparently not knowing that it has been shown that it is incapable of giving correct results as the precipitate is not MnO_2 but a lower oxide. They also give the method of Metzger and McCrackan but do not give the Volhard method which most analysts have found the simplest, quickest and most accurate. They advise the use of aluminum for the reduction of iron but do not mention that commercial aluminum usually contains enough iron to cause a serious error. For zinc they give the Waring method which is the best; but in the presence of much manganese the sulfide separation must be repeated or the separation will not be complete. In the description of the volumetric method for zinc they do not lay enough stress on the necessity of keeping all conditions uniform. Variations in the temperature, acidity and amount of ammonium chloride present, all affect the end point. Except under very unusual conditions the precipitate is a double ferrocyanide of zinc and potassium and there is a whole series of these salts; any slight changes in conditions will cause an unexpected one to be formed.

The third section of the book gives special methods for particular alloys. Except in the cases of copper and spelter no directions are given for sampling. For copper, two or three methods are given, but no preference is expressed and the reader is left in doubt as to which it is better to use. For spelter, the method described is very unsatisfactory; three slabs from a car load is not enough for a sample. Owing to the conditions of manufacture there is necessarily considerable variation in the composition of the slabs from a single cast at one furnace. Not less than five slabs of high-grade or ten of common spelter should be taken. It is much better to saw the slabs than to drill them as the sawdust can be readily mixed and quartered while the drillings have to be cut up and then are difficult to mix.

Larger amounts of material should be taken for analysis than are recommended for spelter. In high-grade spelters, which are largely used by the makers of alloys, there is often not over 0.02 per cent. of iron and 0.03 of lead, and to determine such small amounts with accuracy the sample should consist of ten to twenty grams.

The method given for the separation of manganese and zinc in an aluminum alloy is not good as it has been repeatedly shown that when manganese is precipitated by an oxidizing agent the precipitate is very apt to retain zinc.

In many cases several methods are described for the same separation but there is no criticism of them, and the reader is left to make his own selection without the benefit of the authors' experience.

The book will be found useful by those who have to make occasional analyses of alloys and also by those who are regularly engaged in such work when they come across an alloy of a type with which they are not familiar. G. C. STONE.

Pure Foods. Their Adulteration, Nutritive Value and Cost. By JOHN C. OLSEN. Ginn & Co. 1911. 12mo. 210 pages, illustrated. $0.80.

The author states in the preface that "this volume was not written to meet the needs of the technical chemist;" it is intended rather as an elementary text-book in food chemistry and for the public. As a book for the public it is better than the majority of "popular" books on food in that it is written by a man of scientific training and is not devoted to the exploitation of any fad or "diet system;" but the difficult problem of presenting food values and standards of purity with scientific accuracy in non-technical language is not fully solved.

It must also be said that the volume is too slight a contribution to be of much value for class work in any but the shortest courses and shows neither the exactness of statement nor the sense of proportion as to distribution of space, which is so desirable in an elementary text-book. Twice as much space is given to candies as to bread, cereals, and vegetables together; over four pages are devoted to vanilla and tonka extracts, while less than one page is given to the manufacture and refining of sugar from beets and cane.

As the book is not intended for the class of readers to whom this Journal goes, it is hardly appropriate to take space here to point out specific statements which seem to the reviewer to stand in need of revision.

The outlines of the manufacture of cacao products and of corn starch and corn syrup are good, and the author's many professional friends will anticipate the appearance of a second edition in which the book as a whole is brought up to the standard of these chapters. H. C. SHERMAN.

Plant Food. Its Sources, Conservation, Preparation and Application. By WM. H. BOWKER. pp. 52 Private publication.

This small volume, as indicated by its title, presents a clear statement of the generally accepted ideas concerning the essential elements of plant food, their sources, preparation and use. It commences by outlining the needs of modern farming and the part which fertilizers play in the production of crops.

The author describes at some length the needs of plants, and more especially the three essential elements—nitrogen, phosphoric acid, and potash. Nitrogen is considered of first importance for the reason that it is relatively the least abundant and, therfore, the most costly. "Insoluble" phosphoric acid is considered of little value, contrary to the advocates of ground phosphate rock.

This is followed with several pages giving the usual practice in localities where fertilizers have been used longest and in largest quantities. The amount of fertilizers required for the principal cultivated crops is specified together with notes on the preparation of the land, etc. The author concludes the volume with a chapter on "Commercial Valuations, and Government Regulations." F. B. CARPENTER.

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By D. D. BEROLZHEIMER, Librarian, Chemists' Club, New York.

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RECENT INVENTIONS

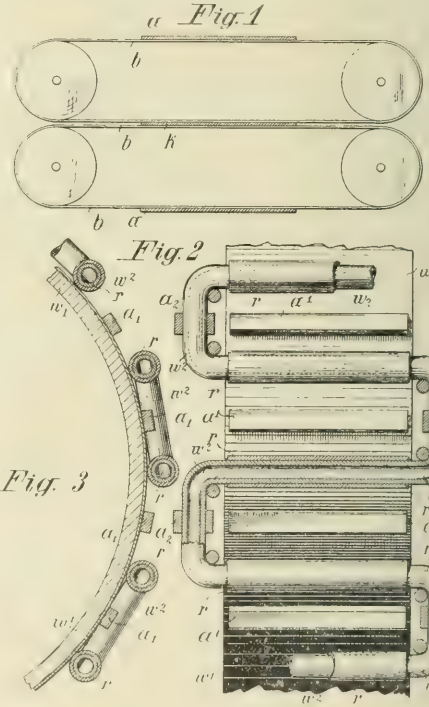
Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

PROCESS FOR THE ELECTROLYTIC DEPOSIT OF METALS.

U. S. Patent No. 1,003,799, to Armin Rodeck, of Milan, Italy.

This invention is a process especially adapted for the separation of metals electrolytically by the aid of mechanism.

There is inserted between an ordinary fixed anode and a movable cathode a mechanically moved transferring mechanism of suitable material, which is either naturally conducting or is made conducting at the operative surface. This mechanism usually receives a porous non-conducting coating of material which serves as a carrier of the electrolyte and adapts itself in its outer form to the shape of the object to be coated. The electric current passes in this process from the anode through the porous material to the transferring mechanism, and from this latter to the cathode, where naturally the quantity of metal depositing upon the transferring mechanism from the anode will at any given moment exactly equal the quantity proceeding from this mechanism to the cathode, because the current strength is throughout the same. It is, therefore, not necessary to make the anode itself of that shape which corresponds to the profile of the article to be coated, but that form of anode which can be obtained most cheaply in commerce as, for instance, bars, rods, sheets, or even scraps can be used by providing them with suitable current connections and pressing them against the transferring mechanism. It, of course, is true, by reason of the fact that the electric current must pass twice through the coating of material which really constitutes secondary electrodes and also acts as a carrier of the electrolyte, that the resistance to transfer is increased. But, on the other hand, in consequence of the wide range of choice of the shape and material of the transferring mechanism, one can so select said mechanism that quite a thin coating, even on a somewhat rough surface of the object to be coated, will effect a perfect deposit; and, therefore, the process can be easily carried on with the ordinary current tension usually employed in the electro-depositing operations.



METHOD OF MAKING AMMONIUM CARBONATE.

U. S. Patent No. 1,004,361, to Julius Bueb, of Dessau, Germany.

In carrying out this process carbon dioxide is caused to pass through the gas moistening, or wash, bottle K^1; at the same time steam is admitted into K^1 through the pipe L in such quantity as to maintain the temperature of the water in K^1 at any point desired between 50° and 100° C. By the passage of the carbon dioxid through the hot water it is heated to the necessary temperature and, in addition, carries with it abundant steam, the latent heat of which also enters into effect during

Fig. 1

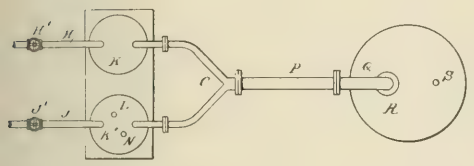
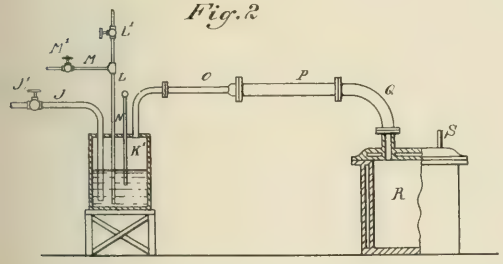


Fig. 2



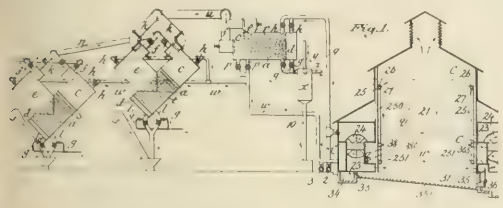
the reaction. Gaseous ammonia is caused to pass through the pipe H and the wash bottle K, which usually is cold, but may be heated in a manner similar to K^1 if desired. The gaseous ammonia, hot carbon dioxide and water vapor pass from the bottles K, K^1 through the branched pipe O into the mixing tube P where they react together, the hot mixture then passing through the connection Q into the cooled sublimate chamber R where the ammonium carbonate is precipitated.

By regulating the temperature of the water, through which the carbon dioxide is caused to pass, it is possible to regulate the quantity of steam according to the percentage of ammonia desired in the cardonate of ammonia obtained. Instead of the carbon dioxide the ammonia, or a mixture of both, can be caused to pass through the hot water.

SALT-MAKING.

U. S. Patent No. 1,006,196, to Herman Frasch, Cleveland, Ohio. Assignor to the United Salt Company, Cleveland.

This invention relates to a process of salt making and to products obtainable by said process. In accordance with the



process, saturated brine of an appropriate temperature is exposed unsupported in the form of drops, to an evaporation promoting atmosphere (in other words, to an atmosphere in which the tension of the water vapor present is less than the vapor tension of the brine exposed thereto) in such manner that the evaporation proceeds more rapidly than the crystallization and that consequently the brine becomes supersaturated, and this supersaturated brine (with or without further evaporation) is allowed to precipitate the salt either while sufficiently quiet to allow the fine grains of salt to settle or while in sufficient motion to keep them from settling or while flowing over a suitable bed (surface) in such volume and at such speed that the fine grains of salt are carried along with the current, or partly in one and partly in another or others of said modes.

The accompanying illustration shows apparatus in which the process is carried out.

PROCESS OF PURIFYING WATER AND SEWAGE.

U. S. Patent No. 1,007,647, to Carl R. Darnall, of Washington, D. C.

This invention relates to the purification of water and sewage, and has for its object the provision of a method and apparatus whereby dry chlorine gas may be used in a practical and efficient manner for purifying water, and the chlorine accurately supplied in the desired quantity to effect the desired result without water or imparting an unpleasant odor to the water.

The process consists in establishing a supply of dry chlorine gas under high pressure, and admitting said gas to the liquid to be treated under a uniform low pressure.

The accompanying illustration shows apparatus in which the process may be practiced.

FIG. 1.

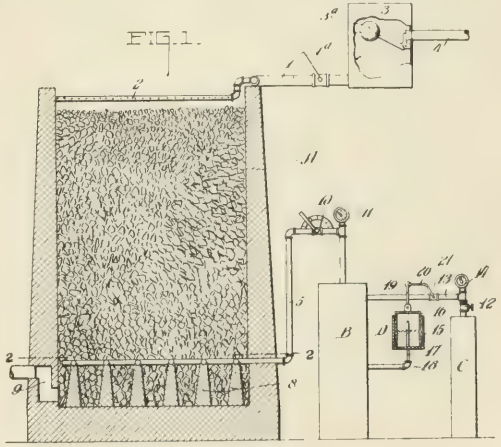
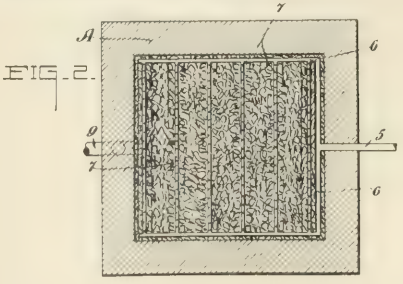


FIG. 2.



MARKET REPORT.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF FEBRUARY.

ORGANIC CHEMICALS.

Acetanilid	Lb.	20 1/2	@	23
Acetone (drums)	Lb.	14 1/2	@	15
Alcohol, grain (188 proof)	Gal.	2.56	@	2.58
Alcohol, wood (95 per cent.)	Gal.	50	@	52
Alcohol, denatured (180 proof	Gal.	40	@	42
Amyl Acetate	Gal.	3.00	@	3.25
Acetic Acid (28 per cent.)	C.	1.79 3/4	@	2.02 1/2
Aniline Oil	Lb.	10 3/4	@	11 1/2
Benzoic Acid	Lb.	23 1/2	@	28
Carbon Tetrachloride (drums)	Lb.	8	@	12
Carbon Bisulphide	Lb.	10	@	14
Chloroform	Lb.	20	@	30
Carbolic Acid (drums)	Lb.	17	@	19
Citric Acid (domestic), crystals	Lb.	38 1/2	@	39
Camphor (refined in bulk)	Lb.	—	@	44
Dextrine (imported potato)	Lb.	5 1/2	@	5 3/4
Dextrine (corn)	C.	2.25	@	2.96
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8 1/2	@	9 1/2
Glycerine (dynamite)	Lb.	15 3/4	@	17
Oxalic Acid	Lb.	7 1/2	@	7 7/8
Pyrogallic Acid (bulk)	Lb.	1.35	@	1.45
Salicylic Acid	Lb.	32	@	34
Starch (corn)	C.	2.07	@	2.68
Starch (potato)	Lb.	5	@	5 1/4
Tannic Acid (commercial)	Lb.	35	@	35 1/2
Tartaric Acid, crystals	Lb.	30 1/2	@	31

INORGANIC CHEMICALS.

Acetate of Lime (gray)	C.	2.25	@	2.30
Acetate of Lead (brown, broken)	Lb	7 3/4	@	8
Alum (lump)	C.	1.75	@	2.00
Ammonium Carbonate, domestic	Lb.	8 1/4	@	8 3/8
Ammonium Chloride, gray	Lb.	5 3/4	@	6 3/4
Aluminum Sulphate	C.	90	@	1.75
Aqua Ammonia (drums) 16°	Lb.	2 1/4	@	2 1/2
Arsenic, white	Lb.	2 3/8	@	2 7/8
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Barium Chloride	C.	1.45	@	1.60
Barium Nitrate	Lb.	4 3/4	@	5
Borax, crystals (bags)	Lb.	3 1/2	@	4
Boric Acid, crystals	Lb.	7	@	7 1/2
Bromine, bulk	Lb.	25	@	30
Bleaching Powder (35 per cent.)	C.	1.22 1/2	@	1.30
Barytes (prime white, foreign)	Ton	18.50	@	22.50
Blue Vitriol	Lb.	4.90	@	5 1/4
Calcium Chloride	C.	65	@	90
Chalk (light precipitated)	Lb.	4 1/2	@	6
China Clay (imported)	Ton	11.50	@	18.00
Feldspar	Ton	7.00	@	9.00
Fuller's Earth, powdered	C.	80	@	85
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1.15	@	1.55
Iodine (resublimed)	Lb.	2.60	@	2.65
Lead Nitrate	Lb.	8 1/8	@	8 5/8
Lithium Carbonate	Lb.	67	@	70
Magnesite (raw)	Ton	7.50	@	8.50
Nitric Acid, 36°	Lb.	3 7/8	@	4 1/4
Phosphorus	Lb.	35	@	90
Phosphoric Acid, sp. gr. 1.75	Lb.	22	@	26
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bromide	Lb.	31	@	34
Potassium Permanganate (bulk)	Lb.	9 1/4	@	10
Potassium Cyanide (bulk) 98–99 per cent.	Lb.	19 1/2	@	21
Potassium Iodide (bulk)	Lb.	2.10	@	2.15
Potassium Chlorate, crystals	Lb.	8 1/4	@	9 1/2
Potassium Nitrate (crude)	Lb.	4 1/2	@	5
Potassium Bichromate, 50°	Lb.	6 7/8	@	7
Quicksilver	Flask	47.00	@	49.00
Salt Cake (glass-makers')	C.	55	@	65
Silver Nitrate	Oz.	36 7/8	@	39 1/2
Soapstone in bags	Ton	10.00	@	12.00
Sodium Acetate	Lb.	4 1/4	@	5
Sodium Chlorate	Lb.	8 1/4	@	9 1/2
Sodium Bicarbonate (English)	Lb.	2 3/4	@	3
Sodium Bichromate	Lb.	5	@	5 1/4
Sodium Hydroxide, 60 per cent.	C.	1.70	@	1.75
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent., spot	C.	2.16	@	2.20
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	6 7/8	@	7 5/8
Sulphur, Roll	C.	1.85	@	2.15
Sulphur, Flowers (sublimed)	C.	2.20	@	2.60
Sulphuric Acid, 60° B	C.	85	@	1.00
Talc (American)	Ton	15.00	@	20.00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	12 3/4	@	13
Tin Oxide	Lb.	47	@	51
Zinc Chloride (granulated)	Lb.	4 1/4	@	4 1/2
Zinc Sulphate	Lb.	2 1/4	@	2 1/2

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	40	@	45
Black Mineral Oil, 29 gravity	Gal.	12	@	12 1/2
Castor Oil (No. 3)	Lb.	9 1/2	@	10 1/2
Ceresin (yellow)	Lb.	8	@	14
Corn Oil	C.	5.45	@	6.00
Cottonseed Oil (crude), f. o. b. mill	Gal.	31 1/2	@	34 1/2
Cylinder Oil (light, filtered)	Gal.	19 1/2	@	20
Japan Wax	Lb.	9	@	9 1/2
Lard Oil (prime winter)	Gal.	80	@	85
Linseed Oil (double-boiled)	Gal.	73	@	76
Paraffine Oil (high viscosity)	Gal.	23 1/2	@	24
Paraffine (crude 120 & 122 m. p.)	Lb.	3	@	3 1/8
Rosin Oil (first run)	Gal.	36	@	—
Spindle Oil, No. 1	Gal.	14	@	14 1/2
Sperm Oil (bleached winter) 38°	Gal.	76	@	78
Stearic Acid (double-pressed)	Lb.	9 1/2	@	9 3/4
Tallow (acidless)	Gal.	63	@	65
Tar Oil (distilled)	Gal.	30	@	31

METALS.

Aluminum (No. 1 ingots)	Lb.	19	@	19 3/4
Antimony (Hallet's)	Lb.	7 3/8	@	7 1/2
Bismuth (New York)	Lb.	2.10	@	2.15
Copper (electrolytic)	Lb.	14	@	14 3/8
Copper (lake)	Lb.	14.05	@	14 1/2
Lead, N. Y	Lb.	—	@	4
Nickel	Lb.	40	@	45
Platinum (refined)	Oz.	45.50	@	46.00
Silver	Oz.	55	@	59 3/8
Tin	Lb.	43 1/2	@	44 1/2
Zinc	Lb.	6.40	@	6.60

FERTILIZER MATERIALS.

Ammonium Sulphate	C.	3.26	@	3.30
Fish Scrap, domestic, dried	Unit	3.25	@	10
Blood, dried	Unit	3.00	@	—
Tankage, high grade	Unit	2.85	@	10
Bone, 4 1/2 & 50, ground, raw	Ton	27.00	@	—
Potassium, "muriate," basis 80 per cent.	Ton	38.05	@	—
Phosphate, acid, 16 per cent.	Ton	—	@	8.00
Phosphate rock; f. o. b. mine:				
Florida land pebble 68 per cent.	Ton	3.70	@	3.80
Tennessee, 68–72 per cent.	Ton	4.25	@	4.50
Pyrites, furnace size, imported	Unit	0.13	@	0.13 1/4
Castor meal	Unit	2.95	@	3.10 & 10
Mowrah meal	Ton	8.50	@	9.00

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume IV APRIL, 1912 No. 4

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Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered at the Post-Office, Easton, Pa., as Second-class Matter.

TABLE OF CONTENTS.

EDITORIALS:

The Purification and Softening of Water by Permutite. 240
The Paint and Varnish Industry of the United States. 242

ORIGINAL PAPERS:

Carbon Brushes. By W. R. Whitney. 242
The Relation of the Refractive Index of Soda Lime Glasses to their Chemical Composition. By Edwin Ward Tillotson, Jr. 246
A New Method for the Determination of Vanadium. By D. J. Demorest. 249
A Rapid Method for the Determination of Vanadium in Steels, Ores, etc., Based on its Quantitative Inclusion by the Phosphomolybdate Precipitate. By J. R. Cain and J. C. Hostetter. 250
A New Method for the Determination of Vanadium; an Explanation. By J. R. Cain and D. J. Demorest. 256
The Rapid Determination of Vanadium in Steel. By Frank Garratt. 256
The Direct Determination of Small Amounts of Platinum in Ores and Bullion. By Frederic P. Dewey. 257
The Determination of Moisture in Coals. By E. H. Archibald and J. N. Lawrence. 258
A Method for the Utilization of Lead Furnace Fume. By L. S. Hughes. 262
A Method for Testing Out Problems in Acid Phosphate Manufacture. By F. B. Porter. 264
On the Determination of Carbon Dioxide in Soils. By Leon T. Bowser. 265
The Phenomenon of the Apparent Disappearance of the Higher Boiling Phenols in Creosoted Wood and its Explanation. By Samuel Cabot. 266
The Fluidity of Fish Oil Mixtures as an Additive Property. By George F. White. 267
Comparative Value of Irrigated and Dry-Farming Wheat for Flour Production. By Robert Stewart and C. T. Hirst. 270
The Influence of Carbon upon Nitrification. By H. W. Clark and George O. Adams. 272
Acidity in Wheat Flour; its Relation to Phosphorus and to other Constituents. By C. O. Swanson. 274
The Chemistry of Anaesthetics, IV: Chloroform. By Charles Baskerville and W. A. Hamor. 278

LABORATORY AND PLANT:

The Adaption of the Centrifugal Pump to Chemical Problems. By F. G. Wheeler. 288
New Forms of Gas Analysis Apparatus. By G. A. Burrell. 297
An Improved Extraction Apparatus. By W. C. Blasdale. 302
Notes on a New Form of Extraction Thimble. By P. A. Bocck. 303

ADDRESSES:

Fertilizer Chemistry A Report of Progress. By Paul Rudnick. 304

CURRENT INDUSTRIAL NEWS.

Progress of the Chemistry of Papermaking. 307
Recent Investigations on Alloys. 307
Siloxide. 308
Extraction with Naphthalene. 308
Fire Extinction. 309

NOTES AND CORRESPONDENCE:

The Centenary of the Introduction of Gas. 309
American Electrochemical Society, Twenty-first General Meeting, Boston, April 18th to 20th. 309
American Commission on Organic Nomenclature. 309
Eighth International Congress of Applied Chemistry. 310
Correction. A Convenient Filtering Apparatus. 310
The Business Aspect of the Kelp Proposition. By Frederic P. Dewey. 311
Importations of Acetic Anhydride. 311

CONSULAR AND TRADE NOTES:

English Municipal Gas Works. 312
Utilization of Natural Gas in Hungary. 312
Swedish Coal Situation. 312
Cork Trade of the United States. 312
Malaysian Tin Exports. 312
Shark's Live Oil Industry Proposed. 312

BOOK REVIEWS:

Transactions of the American Institute of Chemical Engineers; The Technology of Bread-Making, Including the Chemistry and Analytical and Practical Testing of Wheat, Flour and other Materials Employed in Bread-making and Confectionery; Die Chemie der trocknenden Oele. 313

NEW PUBLICATIONS. 314

RECENT INVENTIONS. 315

MARKET REPORT. 316

EDITORIALS

THE PURIFICATION AND SOFTENING OF WATER BY PERMUTITE.

The advantages to be gained by the use of soft water in steam raising and for many manufacturing operations are now generally recognized. It is also conceded that the presence of iron in water for dyeing, printing, bleaching works and paper factories, is very undesirable. In brewing, too, water containing much iron is objectionable. Therefore, the application of the product "Permutite," an artificial zeolite, $3SiO_2.Al_2O_3(K_2O.Na_2O.CaO).6H_2O$, for the purpose of removing certain constituents from water and softening it, is of great interest to the chemist and engineer.

The Permutit-Filter Co., of Berlin, was organized in 1909 for the purpose of exploiting the above-mentioned artificial zeolite under the trade name "Permutite" (see Appelius, *Chem. Rev. Fett-Harz. Ind.*, **1909**, p. 300). This company devised also a process for softening water and for relieving it of iron and manganese (English Patent 26,074, Nov. 9, 1910). A number of other foreign companies are now being organized for developing these methods of water treatment. The "Permutite" process has been operated on a commercial scale at Glogau for the removal of manganese from water.

R. Gans (*Mitt. aus. d. Koenigl. Prufungsanst. f. Wasserversorgung u. Abwasserbeseitigung zu Berlin*, **1907**, p. 8; *Woch. f. Brau.*, **24**, 270) found that the aluminate-silicates exchanged their bases not only for alkalies and alkaline earths, but also for iron, manganese, lead, silver, and presumably for all metals. He pointed out that a filter of such material could be regenerated after use by washing with alkali salts, by which the metals separated from the water were redissolved. According to Gans, by fusing aluminum silicates with sodium carbonate and sufficient quartz to decompose all the carbonate, aluminate-silicates containing 12–15 per cent. Na_2O are obtained which are excellent filtering media. He stated that the soda content was of the greatest importance, since it was found to replace the bases present in the water. In one experiment conducted by Gans, well water which rapidly became turbid in the air, owing to the separation of iron, was filtered through a 10 cm. layer of calcium aluminate, the water level falling 10 cm. per hour. The whole of the iron was removed from the water by the filter, from which it was afterwards dissolved by washing with sodium chloride solution.

Gans also made experiments on the softening of water for boiler-feed purposes. A hard water was treated with sodium aluminate-silicate, which was found to remove the lime and magnesia quantitatively, leaving only the alkali carbonates, sulphates and chlorides, together with the small proportion of silicates contained in the original water. He found that if only three-fourths of the sodium of the sodium aluminum silicate was replaceable, 4.5 lbs. of the material would remove from 30 cu. ft. of water possessing a hardness of 20 degrees (German), all salts capable of forming boiler incrustation. Gans reported (*Chem. Ztg.*, **31**, 355) that manganese could be separated from water by filtration through a layer of granular aluminum silicate, prepared by fusing clay with an alkali carbonate, and adding to the fused mass sufficient quartz to combine with almost the whole of the alkali. After extracting the mass with water, the silicate was obtained in a granular or flaky form. Regeneration of foul filtering layers was found to be accomplished by washing with calcium chloride or calcium-sodium chloride solution. Gans also reported that hydrated silicates, both natural and artificial, were capable of withdrawing the bases from alkaline and neutral salt solutions, and that potash and soda might be eliminated from sugar juice by means of aluminun silicate (*Z. Ver. Deut. Zuckerind.*, **1907**, p. 206). In German Patent 174,097, of January 12, 1905, issued to Gans, it is pointed out that artificial zeolites or alkaline-earth aluminate-silicates for the purification of molasses need to be free from uncombined lime (see also French Patent 374,525, February 11, 1907, of the J. D. Riedel A.-G.; and United States Patent 943,535, December 14, 1909, of R. Gans, for the manufacture of hydrated aluminum silicates).

In a patent issued to Gans in 1907 (English Patent 8232, April 9, 1907) the claim is made for the manufacture of hydrated alumino-silicates, or artificial zeolites. About this time Gans gave further evidence of the usefulness of aluminum silicates for improving water supplies (*J. Gasbeleucht.*, **50**, 1026); he pointed out that iron and manganese were removed completely by passing the water through a filter composed of calcium-aluminum silicate; that a hard water could be softened by filtration through sodium-aluminum silicate, the latter material also serving to remove any iron, manganese and ammonia which might be present in the water; and recommended that in supplies where the hardness was due principally to calcium sulphate, the water be passed successively through layers consisting of strontium-aluminum silicate and calcium-aluminum silicate.

In 1908, Lührig and Becker (*Chem. Ztg.*, **32**, 514, 531) conducted experiments on the efficiency of the "Gans method" for removing manganese sulphate from water by means of natural or artificial zeolites. They found that similar results were obtained with the natural and artificial substances, but that the latter were more active; that a given quantity of manganese sulphate was most effectively removed from dilute solution made to filter slowly through a bed of the silicate; that the presence of the salts of other bases in solution was unfavorable to the absorption of manganese; and that by subsequent treatment of the silicate with solutions of salts such as ammonium chloride, in order to revivify it, the whole of the absorbed manganese was not removed, but was found to be present partly as hydrated peroxide, which, on a large scale, tended to obstruct the filter beds.

The patents granted to R. Gans and the J. D. Riedel A.-G. in 1909 (French Patent 405,990, July 17, 1909; English Patent 21,184, Sept. 16, 1909; and U. S. Patent 951,641, March 8, 1910) contain claims for a process for removing iron and micro-organisms from water. It is stated that the process consists in treating the water with insoluble higher oxides of manganese with the coöperation of natural or artificial zeolites (cf. German Patents 145,797 and 154,792). The claim is made that if a calcium-zeolite is treated with a solution of a manganous salt, a manganese zeolite is formed, which, on treatment with a solution of calcium permanganate, yields a product consisting of the higher oxides of manganese distributed in a fine state of division throughout a calcium-zeolite. According to Gans (*Chem. Ind.*, **32**, 197), 450 kg. of calcium-zeolite were found to be changed, by washing with manganous chloride solution, to manganese-zeolite; treatment with a calcium manganate solution converted the latter into calcium-zeolite again. On filtering the water to be treated through this material, the iron is said to be rapidly oxidized and removed, and the bacteria and organic matter destroyed; any manganese present in the water is also said to be removed. In later patents to the same parties (French Patent 409,006, Nov. 13, 1909; English Patent 26,842, Nov. 18, 1909; and U. S. Patent 960,887, June 7, 1910), the water to be softened is treated with barium, calcium or magnesium hydroxide, and sodium hydroxide or carbonate, according to the nature of the hardness, and then filtered through a layer of a natural or artificial zeolite.

When a water containing manganese salts in solution is passed through a filtering bed composed of a zeolite impregnated with higher oxides of manganese the manganese is separated in the form of a mud. It was found in practice as early as 1907 that if this mud was not removed from the filter, it eventually formed small porous particles which did not interfere with the filtering capacity of the bed, but, in fact, increased its efficacy with regard to the removal of manganese from water (see German Patent 220,609, Oct. 28, 1908, of the J. D. Riedel A.-G). However, when revivification was attempted—*i. e.*, on the bed containing manganese mud—the manganese retained was found to be an obstruction to rapid filtration.

Natural stones, such as trass, phonolite, porphyry, leucite, trachyte, sodalite, and mica, are also employed in making filters through which the water to be treated is passed. These minerals are used either directly, if they have been hydrated naturally, or after they have been treated with steam under pressure; but we are not aware of their application in the place of artificial zeolite.

Two investigations have recently been published on "Permutite." Anders (*Woch. f. Brau.*, **28**, 78) conducted laboratory experiments with the product for the softening of water. His results showed that "Permutite" is applicable for the softening of feed-waters, but not for mash-waters because it takes up sodium salts. He found that a "Permutite" filter may be completely regenerated by the use of a sodium chloride solution. Kolb (*Chem. Ztg.*, **35**, 1393, 1410) also investigated the application of "Permutite" to the softening, as well as the purification, of water. He made experiments, both by shaking and by filtration, as to the interchange occurring between "Permutite" and the chlorides of calcium, magnesium, and potassium, and found that the soda of the "Permutite" was replaced by the bases of the salts added in molecular proportions. He also ascertained that the "Permutite" could be regenerated by treating the used substance with sodium chloride, and that iron and manganese, as well as the alkaline earth metals, could be removed from solution. Kolb stated that with a filter formed of "Permutite," complete softening of water could be effected, but the water must not contain acid or suspended matter. In the case of a muddy water, in addition to blocking the pores of the filter, the mud coated the grains of the filtering material with inert matter and prevented the desired chemical reactions. Kolb considered the regeneration of the "Permutite" by a solution of sodium chloride to be of industrial importance, since it would enable the same filter to be used for an indefinite period. According to his findings, the richness of the treated water in sodium salts is not detrimental to boiler-feed water.

It would seem that "Permutite," to be of value for technical uses, must be of a granular or leafy, easily porous character, such as is obtained by melting together the constituents in definite proportions. The amount of clay is calculated according to the amount of bases. Gans considers that the composition of an ideal zeolite, $2SiO_2.Al_2O_3.Na_2O.6H_2O$, should be approached.

W. A. Hamor.

THE PAINT AND VARNISH INDUSTRY OF THE UNITED STATES.

Up to ten years ago this industry was more or less in an empirical state. Even the manufacture of dry colors, such as chrome yellow, Prussian blue, chrome green, etc., which are purely chemical colors—and the reaction can be figured out molecularly—was carried on by men who had what they thought were secret formulas, and if more of one liquid than another was added, no note was taken of it. The mixed paint industry was also in a somewhat chaotic state, but a few men came to the realization that white lead was not the only pigment, and linseed oil and turpentine not the only vehicles which could be used. The mixed paint consumption to-day amounts to eighty million gallons per year, and such materials as barytes, blanc fixe, lithophone, sublimed white lead, silica, etc., are now regarded as beneficial accessories, rather than adulterants.

With the co-operation of the Department of Agriculture, such vehicles as soya bean and china wood oils are receiving marked attention. China wood oil is to-day such a necessity that the revolution in China, which has brought the price of the oil up to

$1.19 per gallon has made it apparent that the paint and varnish manufacturer must have it at any price.

The shortage in the crop of flaxseed has not produced that tremendous market disturbance which was feared two years ago, for many prominent chemists have published methods for the use of Menhaden fish oil, which in many respects has shown itself to be at least as good as linseed oil.

The same condition has prevailed in the turpentine market, for in March, 1911, when the price reached $1.13 per gallon, the United States Navy decided that for its work a good turpentine substitute made from petroleum would answer its requirements, and the government is now using thousands of gallons of turpentine substitute for which it pays from twelve to fifteen cents per gallon. As the Navy purchased in 1910 about $70,000.00 worth of turpentine, this innovation has had a tremendous effect on the turpentine market, and the chances are it will never see such an abnormally high price again.

There seems to be a difference of opinion, all over the United States, regarding the materials to be used for paint, for it is conceded that paint should be made for the purpose for which it is intended, and should not necessarily be made of the highest priced materials which will produce that result. The Battleship Gray which the Government has partially adopted for the navy is made of 45 per cent. zinc oxide and 45 per cent. barium sulphate, with the necessary tinting material to produce the shade. A paint made of such materials costs about 25 per cent. less than the lead and zinc paints which were formerly used. The results showed that the zinc oxide and barium sulphate paint dried with a harder film, and was not affected by salt water as much as the lead paint formerly used.

A similar condition of affairs has developed in the maintenance departments of the large railroads of the United States, and they have come to realize that no single pigment is as good as a mixture of pigments, and no single pigment is as good as a pigment which contains a reinforcing material in limited amounts.

The trend of opinion among paint manufacturers seems to be that they are more inclined to talk freely than they have been heretofore. Twenty-five years ago a paint manufacturer regarded a formula which he had as a valuable secret, but chemists who have made a specialty of the analyses of paints and their syntheses have shown that the average pigment mixed with oil, dryer and a volatile thinner is not a difficult mixture to analyze, and many of the secrets of the ignorant paint manufacturers have been exposed for their own benefit. Instead of having what they thought were valuable secrets, they had in many instances only mediocre formulas, which they improved when they saw what their competitors were doing.

Paint is so largely an engineering material that a knowledge of its composition is not to be treated lightly, and must not be regarded as an extravagance. Paint for decorative purposes presents new problems. The question of hygiene has entered so much into the use of paint that the wall paper manufacturers in England are now going into the manufacture of interior wall paints because people want washable walls in preference to those which harbor filth and germs.

MAXIMILIAN TOCH.

ORIGINAL PAPERS

CARBON BRUSHES.

By W. R. WHITNEY.

Received January 24, 1912.

The object of this paper is to describe some experiments which are being carried out with the view of assisting in an improvement in the qualities of motor and generator brushes, particularly of the carbon type. It is well known that while there have been very many improvements in all sorts of electrical apparatus during the past twenty years, there has not been a corresponding improvement in the quality of brushes, at least in this country. It is a peculiar commercial or manufacturing condition which all engineers will recognize when their attention is called to it—that an electrical manufacturing company usually puts upon its motors and generators all the legitimate accessories of its own make which are possible, excepting the brushes, and forces the users to purchase brushes from companies not necessarily in very close touch with electrical requirements.

If the brush was as simple an article of manufacture as the lag screw with which the apparatus is attached to the floor, this would not be serious, but quite a different condition exists. In fact, I think it is safe to say that a poor carbon brush, or brush of a wrong type, may render inoperative any kind of electrical apparatus. When one considers the stoppage of a long line of electric cars or the temporary shut-down of a generating plant, because of defects in a brush, one wonders that the demands have not already made an art of brush-making. One finds, in fact, that the production of this very essential, unobtrusive little block of carbon has had hardly any study at all.

Every electrical machine is carefully designed in detail as to size and shape of copper, iron and insulation, all of which vary with each machine, but as yet the important characteristics of a brush are not included in the design, although some one grade of brush is expected to operate satisfactorily over a great range of design. As long as this unfortunate condition exists, the best that can be hoped for is a brush which will do fairly well for a large number of machines, very well on a few and cause continuous trouble on a small balance until investigation of the constants of the particular machine, or its operating condition, shows the need of a different type of brush.

The careful investigation now in progress leads us to hope that the various characteristics of carbon

brushes will soon be sufficiently understood, so that before long the designers of dynamos and motors will be enabled to use a brush exactly fitted to a particular design of machine, rather than a brush which does fairly well on machines of that general size and character.

Apparently the carbon brush was first made from such stock as is used for arc lamp electrodes and dry cell carbons. It was mixed, molded and baked in practically the same way, and the prices fixed on that basis. We have experimented with the understanding that a product might be producible which could bear a ten-fold greater cost of production than ordinary carbon brushes, and it is probable that our present methods are not far from this condition.

In what we call the early days, the motor or generator brush consisted of a brush of leaves of copper, and this had to be treated with the best of care. It was frequently cleaned and oiled and on some types of machines gave much trouble. It was usually set at an angle, so that the ends of the laminae bore upon the commutator. Any reversal of direction of rotation, as has frequently to take place in such apparatus as railway motors, was out of the question with this kind of brush. A block of solid copper bearing directly upon the commutator on such machines causes arcing and spattering of the metal, as there is a relatively high current passing from one commutator segment to the adjacent segment, through that part of the brush which connects them. This was a reason for laminae in the brush.

Our first experiments were taken up along the line of previous methods of manufacture and attempts were made to get at some sort of life tests and standards of comparison. We tried to learn what a good brush had to do and how long it might be expected to do it. In lamp manufacture the testing is an art by itself. An incandescent lamp is made to burn a certain time at a prefixed efficiency. We questioned whether a carbon motor brush could be submitted to similar life and quality tests. We recognized the importance of learning, if possible, what physical properties or constants for brushes would help in determining quality for electrical uses. The art is undeveloped, so that there is no considerable agreement between engineers even on important points. For example, it would be made clear by one engineer that a brush must be much softer than copper, so as not to wear away the commutator, and must not contain any hard spots because these might take up metal from the commutator. Against this was the equally powerful argument that the brush must be harder, so as to cut mica, and prevent the insulation finally protruding above the copper, and for this reason, carborundum, the hardest practical material, has been experimentally introduced into brush material. That the contact resistance should be relatively high and the body resistance low, were also practical suggestions. In order to operate systematically, we attempted to choose properties or tests to which numerical values could be attached. It was not assumed that all or even any of these factors could be interpreted strictly in terms of brush quality, but some such system of coordinating and comparing experimental products seemed necessary. We would naturally welcome suggestions leading to better tests. There were finally adopted measurements of hardness, tensile strength, density, electrical resistivity and such mechanical tests as chip and fracture tests.

The hardness is determined by the Shore Sclerescope, which consists essentially of a diamond-pointed weight which falls freely in a perpendicular glass tube and, striking upon the brush, rebounds to a height in the tube, which height is read from a scale. In general, the harder the material, the higher will be this rebound. In the case of brushes it distinguishes qualities over a range of about seventy units and is of considerable value in determining regularity of product.

A brush as made for railway motors and containing coke, graphite, lampblack, and binder carbon, if properly baked and fired, would have a hardness about 50, while if the firing be interrupted at say 500° C., its hardness value would be about 20. If the coke and lampblack be omitted, while the binder carbon is 3 per cent., and natural graphite be used, the hardness value will fall to about 16, even after firing for maximum hardness. In other words, such brushes as find common use on electrical apparatus may vary in hardness, depending upon the desired use, from 15 to 75 units of hardness.

The tensile strength is determined by cutting from the brush, held between steel guide plates, a definite testing piece of the carbon which can be held in the grip of the strength-testing machine and which will break at a point where the cross-section is exactly one-quarter square inch. The break is produced by the addition of shot at a definite rate to a pan supported by the test sample. The strength is expressed in pounds per square inch section.

The density compared to water is calculated from the weight of the brush and its physical dimensions.

The resistivity is determined by measuring the voltage drop across contact points $1^1/_2$ inches apart, which points bear heavily upon the brush when a current is sent through the brush. Separate contacts are used for the current. The accuracy of the measurement is about 3 per cent. of itself.

Some sort of chipping test seemed desirable because brushes in use often deteriorate and wear away, due to flaking off of chips from the edges of the bearing surface. This would be expected from the nature of the impacts given a brush when it chatters on a rough armature, revolving at high peripheral speed. The chip test we have used consists in a clamp for holding the brush firmly on a solid base or anvil, and in a weight guided by perpendicular rods, which weight falls from a fixed height and strikes the bearing face of the brush repeatedly at the same point, about a millimeter from the edge. The number of impacts necessary to force off a chip is called the chip test. This is quite surprisingly uniform for uniformly made brushes. It is usually weighted so that a brush of best quality will regularly chip after about 10 impacts

of the weight when dropping from an increasing height in steps of 1 centimeter each.

Additional qualitative tests have resulted from comparison of product under different conditions. For example, the fracture or appearance of the fresh surface produced by breaking the brush across its longer dimensions discloses very effectively any irregularities produced by improper baking or pressing. This cross-section should be quite homogeneous and the fracture regularly conchoidal or square. No shelves, cracks or angular markings will be disclosed on breaking a well made brush. It is believed that such internal irregularities represent weakened structure, that even miniature cracks might take up and carry copper from the commutator and that breaking of a brush in use may often be attributed to internal cracks produced in the manufacture. Undoubtedly a rough commutator or heavy pressure of the spring of the brush-holder accounts for the breakage of many brushes in use, but in our tests on operating machines these variables are kept under control as much as possible.

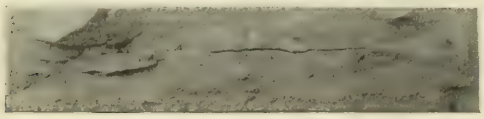

FIG. 1.

FIG. 2.

To illustrate this point, Figs. 1 and 2 are introduced. No. 1 shows a typical case of an improperly baked brush. The ingredients are the same as in 2, which was pressed and baked with greater care. The imperfections noted in 1 are produced by too rapid heating. They are not discoverable in the brush before breaking it. Neither of these is a squirted brush (*i. e.*, cut from a bar squirted through a die), both having been pressed to the desired shape from the powdered mixture.

The composition of the mixture from which the brush is molded has been varied greatly to suit various requirements, but, in general, it is made up of two or more of the four elements: lampblack, finely ground petroleum coke, graphite and some kind of tar or petroleum pitch which serves as a binder.

The effect produced by each of these ingredients is a different one; a suitable balance seems necessary and varies with the use of the brush. A brush made mostly of lampblack alone, with suitable binder, would be dense and hard, but of poor conductivity, and would cut copper badly. One made mostly of graphite is usually too soft and on ungrooved commutators, wears away too rapidly. The mica between the bars gradually protrudes and cuts the brush. Its electrical resistance is very low. One made mostly of coke is hard and of high resistance. It usually cuts the copper badly. The petroleum coke is used because of its uniformity and freedom from mineral matter. It can readily be appreciated that for some special purposes it may be well to incorporate hard polishing material into a brush, as where much mica has to be cut and where high conductivity and, therefore, much graphite is desired. The accidental grains of sand or such mineral impurities as often occur in ordinary coke, on the other hand, are to be carefully excluded.

It might seem that by using the above four forms of carbon (for the pitch leaves a fourth form of carbon, after the heat treatment), a satisfactory product could be obtained, and it has become apparent that the qualities may be varied over a wide range by proper variation of material; but the requirements are continually advancing, so that all sorts of experiments in composition, such as adding sulphur, special oils, etc., have been carried out.

It may be stated as a general rule that except for special conditions, the finer the state of subdivision of the brush ingredients, the better the quality of the finished brush. We have found, after having used ball mills, that the Raymond impact grinder pulverizes coke and similar materials very perfectly. We have found it desirable to grind not only the coke, but also the mixture of all the ingredients, to insure thorough mixing and a dense brush.

The finely divided materials, coke, lampblack and graphite, are placed in a mechanical dough mixer and a solution of the pitch in benzole is added and the whole kneaded for several hours. The benzole is then driven off by heat and the dried product, which is quite hard, is reground to about 200-mesh; this powder is compressed into brush form, in steel molds.

It was first thought that the best way to form the brush was to squirt bars of the mixture by means of an hydraulic press. These bars could then be cut to desired length. So far as our work went along this line, the product was not as satisfactory as when the brushes were individually pressed. Experiments were made in which various proportions of pitch binder were used. The temperatures of the press, mold and brush material were carefully controlled; special presses were built, etc., but irregularities often appeared in the product. The tendency of the material to flow unequally within itself during the passage through the die seemed to be responsible for cleavage planes and internal curved surfaces, which would often not develop until the brush was completed by baking and even then could be disclosed only by breaking the brush. We do not mean to conclude that a satisfactory brush cannot be made by squirting the hot mixture through a die, as the reverse is probably true, but for our purposes we finally adopted the accurate weighing of the mixture for each individual brush and the compression of this weighed material to an exact size in a mold under such a high pressure

that additional pressure produces no further change. This pressure, for a standard railway motor brush, is about 25,000 lbs. per square inch. Above this pressure the quality is not appreciably affected; much below it, inferior product results as shown by density, resistance and strength. Marked effect is produced by variation in the temperature at which the mixture is pressed. For this reason care is taken to have the pressing done at about 25° C.

The pressed brushes are then packed in cast iron boxes, in lots of 100–200, and covered with a liberal layer of fine coke. A cast iron cover which fits the box well is then inserted and this, in turn, is covered with coke dust. A pile of these boxes is shown in Fig. 3. This box fits snugly into the electrically heated muffle shown in Fig. 4.

FIG. 3.

FIG. 4.

Early in the investigation it became evident that a large part of the irregularity of product, the shrinkage-cracks, etc., were to be attributed to a too rapid rate of rise of temperature during the early stages of heating the pressed brush. The pitch, or binder, which on its fractional distillation leaves the cementing carbon, which in turn largely determines the hardness and strength of the brush, is a mixture of organic compounds which liquefies at moderate temperature (100° C.) and rapidly evolves gases far below red heat. This led us to test methods of electric heat, and the rate of distillation of the volatile materials at gradually rising temperature was determined. This work resulted finally in the adoption of a very small type of muffle, for commercial production, which had a capacity for not over 200 brushes. It was heated by a special resistance wire and the temperature controlled by a thermo-element and resistance, so that the rate of rise of the temperature on each lot of brushes was about 5° C. per hour over a period of about 100 hours. The distillation of the binder under this treatment does not rupture or weaken the brush.

When large volumes of brushes are heated or the heating of small containers in a large furnace of usual type is carried out, the brushes near the walls receive a very different heat treatment from those near the center of the furnace. This causes much irregularity of product so that we still give all brushes the first firing or baking in the small wire-wound and heat-insulated muffles, of which No. 4 is an illustration.

FIG. 5.

Fig. 5 shows a double row of these muffles with their control resistances. These latter enable the operator to gradually raise the temperature in each muffle. The rate of this rise is learned by means of pyrometer couples inserted into the muffle. In this, which is a preliminary heating only, the temperature rises during 100 hours to 500° C. In this process the volatile products of distillation have been so slowly eliminated from the brush that no striae, laminations, splits or blisters are produced. The brush is now bound together by a material largely carbon, but still capable of further shrinkage, hardening and decomposition by higher temperature.

After the preliminary heat at 500° C. the brushes are unpacked and a series of tests show relatively inferior qualities throughout, about as follows, for one type of railway motor brushes:

Hardness.	Tensile strength.	Resistance.
20	900 lbs. per sq. in.	0.043 ohm per inch cube

The material can still shrink greatly and improve by a higher heat treatment. This is accomplished in an ordinary porcelain kiln at about 1,400° C., the brushes being packed as before, though not in iron, but in fire clay containers or saggers, the whole being covered with coke dust and the cover carefully luted on. The slightest carelessness in this protection process causes a softening of the outer surface of the brush, where a little combustion has removed the binder-carbon. This binder-carbon is still combustible in the presence of an excess of coke powder.

Owing to the severe requirements for railway motor brushes, the work for a long time was devoted exclusively to this field and there is probably still plenty of improvement possible.

As the work has advanced, the refinements of requirements have become more and more apparent, and it is quite evident now that several different carbon brush types are necessary to satisfy the requirements for different types of machines. In case of this particular brush, however, it is worth attention that by slight modifications in the process, such as fineness of grinding, pressure on the hydraulic press, etc., the record of tests kept during the past 2 years shows the following changes:

	Hardness.	Resistance.	Tensile strength.
1909.....	52.3	0.00135	1800
1911..	58–60	0.00120	2700

Attempts were made to operate without change in the components, as weighed out; all qualities have improved through small refinements.

Development of the railway brush led to trying the same product on other types of electrical apparatus, and it was at once evident that the general brush requirements call for more than one kind of brush and more than a single composition. Generator brushes, while they do not meet the severe conditions met by railway motor brushes and may therefore be softer and of lower physical tests, should have high conductivity and should in use develop a polished commutator without cutting or smutting the metal. A fairly satisfactory type of generator brush may be made almost entirely of ash-free graphite and binder-carbon and will have approximately the following values on test: Hardness, 35; resistance, 0.00078; tensile strength, 2500; chip test, 6. It has been found that a brush needs some lubrication qualities which are difficult to express quantitatively. In the past it has even been customary to treat some brushes with oils, vaseline, etc., to give them this lubricating effect. It has also been found possible to improve operation of a commutator by using hard, strong, non-lubricating brushes and to interpose in several of the brush-holders a pure graphite brush, which serves to give desired lubrication for the other brushes. This has led to experiments on a combination brush, of which a section is shown (Fig. 6). In this case, by a proper selection of proportions of binder or pitch and the mixture, it has become possible to gain the same

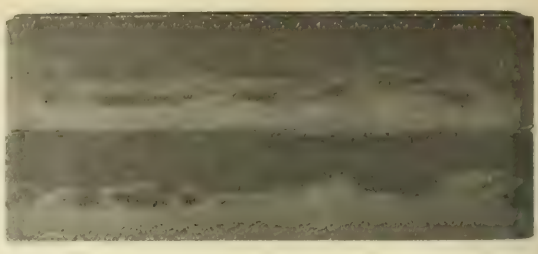

FIG. 6.

shrinkage in the two widely different materials, a hard brush body and a body largely composed of graphite. A sort of laminated brush is thereby produced and if there were service demands for such laminated brushes they could be produced.

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THE RELATION OF THE REFRACTIVE INDEX OF SODA LIME GLASSES TO THEIR CHEMICAL COMPOSITION.

By EDWIN WARD TILLOTSON, JR.

Through the researches[1] of Abbe, Schott, Winkelmann and others, it has been shown that many of the physical constants of glasses may be roughly calculated, with the aid of empirical factors, from their chemical composition. In all of those calculations it was assumed that the constant of the glass was the additive sum of the empirically determined constants of the oxides present, and it was shown that these empirical constants, since they must contain an element characteristic of the manner in which the oxide is combined in the glass, may be very different from the constant of the corresponding pure oxide. No data was presented for calculating the refractive index, although, both from the scientific and industrial standpoints, it is one of the most valuable of constants.

Many expressions for the relation of the refractive index to the density of a substance have been developed, but only two have theoretical significance. The first of these, $\frac{N-1}{d} = K$, was proposed[2] by Gladstone and Dale and the second, $\frac{N^2-1}{N^2+2} \times \frac{1}{d} = K$, was simultaneously and independently developed by Lorenz[3] and Lorentz.[4] In both of these expressions K, the specific refractive power, is a constant which is supposedly independent of the temperature, and which is defined by the chemical composition and constitution of the substance. Many exceptions to this rule occur, however, and the expression of Gladstone and Dale fails completely when the vari-

[1] "Jena Glass and its Scientific and Industrial Application," Hovestadt.
[2] *Phil. Trans.*, **337**, 1863.
[3] *Wied. Ann.*, **11**, 70 (1880).
[4] *Ibid.*, **9**, 641 (1880).

ation of temperature is sufficient to produce a change of state in the substance. Both expressions hold fairly well, however, for liquids and solutions. In a solution or a homogeneous mixture of liquids, which do not react to form a compound, the specific refractive power is an additive function of the respective refractivities of the compounds present and may therefore be calculated as follows:

$$K = \frac{p_1 K_1}{100} + \frac{p_2 K_2}{100} + \frac{p_3 K_3}{100} + \ldots\ldots$$

in which p_1, p_2, p_3, etc., are the percentages in which the several compounds are present, and K_1, K_2, K_3, etc., are their respective specific refractivities.

Very few attempts have been made to apply this relation to glasses or to pure silicates. Larsen[1] has shown by some very accurate measurements on carefully prepared silicates that the specific refractive power is additive within limits of error in case of mixtures of calcium and magnesium metasilicates, and of albite and anorthite, both in the vitreous and the crystalline form. A marked difference, however, occurs in the values of the specific, refractive power for the vitreous and crystalline compounds of like composition.

This paper is an account of an investigation on the refractive index and the specific refractive power of some soda lime glasses for the purpose of obtaining data, whereby these refractive indices might be calculated from their composition with a fair degree of accuracy. The glasses were prepared from pure sodium carbonate, pure calcium carbonate and a high grade of glass sand which analyzed 98.5% SiO_2, the remainder being chiefly aluminum oxide and moisture. The ingredients were carefully weighed out, well mixed and finally fused in clay crucibles in an oxidizing atmosphere of a gas furnace. When the glass was "plain" it was poured out on cold iron plates and, after annealing, was broken into small fragments. The refractive index for white light was measured with the aid of an Abbé refractometer using selected fragments of the glass which presented a smooth, flat surface of the original plate. With a little care in selecting plane fragments of the glass, the values of the refractive index for successive plates usually agreed to within two or three units in the third decimal place, and the average of a number of readings was finally taken.

It is evident that, in the procedure as set forth, there are several chances for error. The glass could not be obtained free from striae in one or even two fusions when clay crucibles were employed, owing to the solvent action of the glass on the crucible; and the melts were stirred very little, therefore, in order that as few impurities as possible should be introduced. It is improbable that the lack of homogeneity, as shown by striae, introduced a very marked error, since the refractive indices of successive preparations[2] of the same glass, measured on carefully ground and polished plates, agreed to within two units in the third decimal place. That this is within the limit of error for glass prepared in clay crucibles is shown by the fact that, even in the manufacture of optical glass, which must possess homogeneity to the highest degree, it is customary[3] to find a difference in a large plate amounting to several units in the fourth decimal place and not uncommon to find a difference of one unit in the third decimal place, and also by the fact that manufacturers cannot vouch for the refractive index of a crown glass to within two units, or for a flint glass to within six or eight units in the third decimal place. The errors arising from preparation and from optical measurements are therefore probably small in comparison to those introduced into the values of the specific refractivities by the use of the calculated densities. It has been shown in a previous paper[3] that the densities of many glasses may be calculated with a moderate degree of accuracy, from the chemical composition. The average error in these computed densities was about one per cent., but occasionally amounted to two per cent. An error of one per cent. in the density produces an error in the refractive index, when it is about 1.5, of five units in the third decimal place, and about one unit in the second place when it is 1.6. In the specific refractivity (Lorenz and Lorentz), one per cent. error in the density introduces an error of from 0.0005–0.0010. It is also possible that an additional error was introduced in the composition of the glasses. No analyses of the glasses were made, but the composition was assumed to correspond to that of the "batch." This error is doubtless small in comparison with other errors since Kultascheff[4] has shown that, although the loss on heating pure sodium metasilicate may amount to 4%, as the percentage of calcium silicate increases the loss rapidly decreases and becomes negligible; and Day and Allen[5] apparently did not observe any noticeable volatilization in the synthesis of feldspar.

The results which were obtained are given in Table I. The first four columns of this table show the composition of the glasses, which correspond to mixtures ranging from $Na_2O.3SiO_2$ to $CaO.SiO_2$. In the fifth column are given the densities as calculated[6] from the composition; in the sixth, the observed refractive index for white light; and in the seventh, the values of K which were calculated from Gladstone and Dale's formula.

When these values for K are plotted in a system, in which the ordinates represent the composition and the abscissas the specific refractivities, as shown in Fig. 1, it becomes evident that they form two straight lines which intersect at a point corresponding to a glass of the composition $2Na_2O.3CaO.9SiO_2$. This break in the curve, therefore, indicates the existence of a compound at this point. It is especially significant since both Kultascheff[7] and Wallace[8] have

[1] *Am. J. Sci.*, **28**, 263 (1909).
[2] Unpublished data.
[3] Zscholke, *Zeit. für Instrumentenk.*, **29**, 286.
[3] Hovestadt, *loc. cit.*, p. 18.
[3] Tillotson, THIS JOURNAL, **3**, 897 (1911).
[4] *Z. anorg. chem.*, **35**, 187 (1903).
[5] "The Isomorphism and Thermal Properties of the Feldspars."
[6] Hovestadt, *loc. cit.* Tillotson, *loc. cit.*
[7] *Z. anorg. Chem.*, **35**, 187 (1903).
[8] *Ibid.*, **63**, 1 (1909).

TABLE I

$CaSiO_3$ mol Per cent.	SiO_2 Per cent	CaO Per cent.	Na_2O Per cent.	D calc	N obs	K obs	K calc.	N calc	N calc.-obs.
00	74.45	0.00	25.55	2.37	1.5000	0.2110	0.2110	1.5000	0.0000
10	73.60	2.50	23.90	2.395	1.5060	0.21127	0.2111	1.5055	—0.0005
20	72.32	5.18	22.50	2.42	1.5115	0.21137	0.21118	1.5111	—0.0004
30	70.85	8.25	20.90	2.45	1.5172	0.21110	0.21125	1.5175	+0.0003
40	69.30	11.70	19.00	2.48	1.5240	0.21129	0.21135	1.52410	+0.0001
50	67.40	15.60	17.00	2.52	1.5334	0.21166	0.2115	1.5330	—0.0004
50	67.40	15.60	17.00	2.52	1.5300	0.21032	0.2115	1.5330	+0.0030
60	65.20	20.20	14.60	2.57	1.5432	0.21137	0.2116	1.5438	+0.0006
70	62.75	25.35	11.90	2.63	1.5590	0.21254	0.2127	1.5594	+0.0004
80	59.60	31.80	8.60	2.705	1.5800	0.21442	0.2142	1.5794	—0.0006
80	59.60	31.80	8.60	2.705	1.5796	0.21436	0.2142	1.5794	—0.0002
100	51.85	48.15	.	2.92	1.6281	0.21517	0.2178	1.6307	+0.0027

[1] —N_{Na}— Larsen, *loc cit.*

observed that in mixtures of sodium and calcium metasilicates a maximum melting point is reached at the composition $2Na_2O.3CaO.5SiO_2$. In column 8

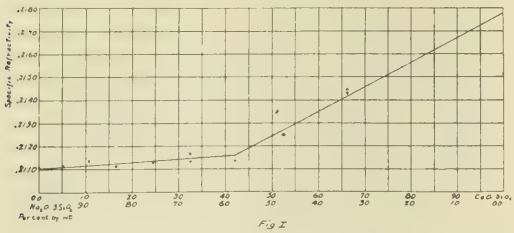

Fig I

(Table I) are given the specific refractivities, as indicated by the two straight lines in Fig. 1; column 9, the refractive index computed from columns 5 and 8; and column 10, the difference between the calculated and observed values of the refractive index.

In Table II are shown similar data for these same glasses, calculated from the formula of Lorentz and Lorenz, and in Fig. 2 the graphic relation of the specific refractivities to the composition. It will be noticed that the same break is observed in the refractive curve as shown by the full lines in Fig. 11.

TABLE II.

$CaSiO_3$ mol. Per cent.	D calc.	N obs.	K' obs.	K' calc.	N calc.	N calc.-obs.
00	2.37	1.500	0.1241	0.12422	1.5006	+0.0006
10	2.395	1.506	0.12406	0.12389	1.5054	—0.0006
20	2.42	1.5115	0.1239	0.12349	1.5110	—0.0005
30	2.45	1.5172	0.12351	0.12361	1.5176	+0.0004
40	2.48	1.524	0.12338	0.12346	1.5244	+0.0004
50	2.52	1.5334	0.12329	0.12323	1.5333	—0.0001
50	2.52	1.530	0.12260	0.12323	1.5333	+0.0033
60	2.57	1.5432	0.12272	0.12300	1.5450	+0.0018
70	2.63	1.559	0.12277	0.12270	1.5586	—0.0004
80	2.705	1.580	0.12305	0.12236	1.5761	—0.0039
80	2.705	1.5796	0.12298	0.12236	1.5761	—0.0035
100	2.92	1.628[1]	0.12155	0.12150	1.6276	—0.0004
	2.43[2]	1.5096	0.12300	0.12291	1.5093	—0.0003

This break is, however, less marked than in the case shown in Fig. 1, and all of the specific refractivities may, for convenience, be considered to lie upon a single straight line indicated by the dotted line in the figure. This behavior of the N^2 formula, that of minimizing the effects of compounds on the specific refractivity, makes it possible to calculate the specific refractivities directly from the percentage composition of the glass. Since the specific refractivity is, within the limits of error, linear, it may be computed by means of the following equation:

$$K = \frac{P_1K_1}{100} + \frac{P_2K_2}{100} + \frac{P_3K_3}{100}, \text{ etc.}$$

in which P_1, P_2, P_3, etc., are the percentages of the oxides, and K_1, K_2, K_3, etc., are the empirically determined specific refractivities of the oxides. For soda lime glasses these are as follows:

SiO_2	0.1220
CaO	0.1210
Na_2O	0.1302

Columns 5 and 6 of Table II show the specific refractivities and refractive indices as calculated by the aid of these factors and column 7 the difference between the calculated and observed values of the refractive index. Not only are the computed values for the glasses given above sufficiently accurate for many kinds of work, but the last glass in Table II shows that the refractive index of glasses richer in silica, may also be calculated with equal accuracy.

Although, in employing this method for estimating the refractive index, no consideration is taken of the compounds which may be formed, yet it is theoretically correct up to the point where the compound is found, and is applicable to the majority of soda lime glasses; for these rarely contain as large a proportion

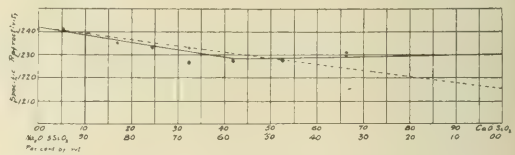

Fig II

of lime as the ratio $2Na_2O.3CaO.xSiO_2$ calls for, and they therefore lie to the left (Figs. 1 and 11) of the break in the specific refractivity curve, and in the region for which the factors, given above, furnish the most satisfactory agreement. It must be remembered, however, that the factors employed represent not the true specific refractivity of the pure oxide, but the true refractivity modified by the nature of the silicate which is formed and also by the inexact values of the density which is employed in the calculations. This is well illustrated in Table III, in which are shown therefractive indices of several oxides, together with the density observed, the density em-

[1] N_{Na} Larsen, *loc cit.*

[2] SiO_2, 77.7%, CaO, 8.5%, Na_2O, 13.8%.

ployed in the computations and the specific refractivities calculated from them, together with the factors given above.

TABLE III.

		N.	D obs.	D calc.	K obs.	K calc.[2]	K[3].
SiO_2	Quartz.....	1.5472[1]	2.652[1]	2.3	0.11961[1]	0.1380	0.1220
	Trydymite..	1.4830[1]	2.318[1]		0.12319[1]	0.1240	
	Fused Quartz	1.4590[1]	2.213[1]		0.12354[1]	0.1188	
CaO.....		1.8320[1]	3.316[1]	4.1	0.13266[1]	0.1073	0.1210

SUMMARY.

1. A series of soda lime glasses have been made and their refractive indices measured.

2. The existence of a double silicate of the type $2Na_2O.3CaO.xSiO_2$, which is doubtless the double metasilicate, described by Kultascheff and Wallace, has been made evident.

3. The specific refractivities of these glasses, computed with the aid of the calculated densities, are additive from pure sodium silicate up to the composition in which the molecular proportion of soda to lime is 2 : 3.

4. Factors have been derived by means of which the specific refractivity of soda lime glasses may be calculated. These are for the formula of Lorentz and Lorenz: SiO_2, 1220; CaO, 1210; Na_2O, 0.1302.

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A NEW METHOD FOR THE DETERMINATION OF VANADIUM.

By D. J. DEMOREST.

Received September 25, 1911.

The following method for the determination of vanadium in steel depends upon the selective oxidation of ferrous sulfate in the presence of vanadyl sulfate by means of manganese dioxide. The vanadyl sulfate is then titrated by adding an excess of permanganate, the excess permanganate being titrated by sodium arsenite.

This differential oxidizing action apparently contradicts the results of J. R. Cain,[4] who found that both iron and vanadium are oxidized, but the reasons for this discrepancy are shown in the note which follows on page 256.

The manganese dioxide should be sufficiently fine to pass through a 200-mesh sieve, and yet should settle in a beaker of water in 30 seconds.

The process in detail is as follows: In a 500 cc. flask a two-gram sample of the steel or iron is dissolved in a mixture of 30 cc. of water and 12 cc. concentrated H_2SO_4 with application of heat. Then one cc. of HNO_3 (sp. gr. 1.42) is added cautiously to oxidize the iron and the solution is boiled for a few minutes to remove the nitrous fumes. Then the solution is diluted with 30 cc. of water and a strong solution of $KMnO_4$ is added to completely oxidize all carbon, etc., and the solution is boiled. If the permanganate or the resulting MnO_2 should disappear, not enough permanganate has been used, and more should be added. Now ferrous sulfate is added to reduce the MnO_2, $HMnO_4$, H_2CrO_4, and H_3VO_4, etc., and the solution is again boiled to remove any possible nitrous fumes. Then pure distilled water is added to make the volume about 250 cc., $N/10$ $KMnO_4$ added until the solution is pink, and the solution cooled to tap water temperature. Ferrous sulfate solution is added until all reducible compounds including chromic and vanadic acids are reduced. Only enough ferrous sulfate should be added to be certain that there is a decided excess present. A solution, one cc. of which equals about 0.01 gram of iron, is the one used. Now about one gram of C. P. MnO_2 is added and the solution shaken vigorously. After two minutes a drop is tested with ferricyanide on a white plate to see if the iron is completely oxidized. It generally takes from four to six minutes. At the end of each minute the solution is tested for ferrous iron until none is present and the shaking is continued for about one-half minute longer. It should be noted that a bluish color will always be obtained in the presence of vanadyl sulfate after the test drop has stood for a few seconds. The end should be taken when the test does not show blue immediately. The blue color which forms after a few seconds, even when there is no ferrous iron present, is due to the reduction of ferri- to ferrocyanide by the vanadyl sulfate. One can become familiar with this end by adding a drop of ferric sulfate containing vanadyl sulfate to a drop of ferricyanide on a white plate.

The MnO_2 oxidizes the ferrous sulfate to ferric sulfate, but does not oxidize the vanadyl sulfate $[V_2O_2(SO_4)_2]$. Then the MnO_2 is filtered off on an asbestos mat, using suction. From a burette a standard solution of $KMnO_4$ is added until a pink tinge is present in the solution, and one cc. more is added, and after one minute the excess permanganate is titrated with Na_3AsO_3 solution. The end point is very sharp. If at this point the operator is not satisfied with this titration, the excess arsenite may be oxidized with $KMnO_4$, ferrous sulfate again added, then oxidized with MnO_2 as before, and the titration repeated, thus giving a check on the titration. A blank determination must be run on a vanadium-free steel, and the result deducted. The blank generally amounts to about 0.00075 gram V. The time required is about one-half hour and the results are very satisfactory. In fact the accuracy is about that of a phosphorus determination.

The vanadium steel standard furnished by the Bureau of Standards was analyzed by the above method. The result of the Bureau chemists is 0.0143 per cent. V and the average of the coöperating chemists is 0.15 per cent. V. The writer obtains the following results, the average being 0.143 per cent.:

0.140	0.138
0.147	0.147
0.143	0.143

To further test the method, two-gram samples of

[1] Larsen, *loc. cit.*
[2] Using Lorentz and Lorenz formula and "D calc."
[3] Factors used in computing specific refractivities.
[4] THIS JOURNAL, **3**, 476 (1911).

vanadium-free steel with the addition of ferro-vanadium containing 0.00684 gram of vanadium were analyzed. The results were 0.00680 and 0.00690 gram V. Another sample with 0.0342 gram V was analyzed, and 0.03432 gram V was found.

To test the effect of chromium on the method, the Bureau of Standards' sample above mentioned was analyzed with the addition of 0.100 gram Cr. The results were 0.143 per cent. and 0.143 per cent. V, showing that chromium has no effect on the vanadium results. Scores of other determinations have been made, proving the accuracy of the method.

The $KMnO_4$ solution used equals 0.001 gram iron per cc., and the arsenite solution has the same strength. This makes the $KMnO_4$ equal 0.000917 gram vanadium per cc. The arsenite solution is made by dissolving about 2.25 grams As_2O_3 in Na_2CO_3 solution and diluting to 2,000 cc.

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A RAPID METHOD FOR THE DETERMINATION OF VANADIUM IN STEELS, ORES, ETC., BASED ON ITS QUANTITATIVE INCLUSION BY THE PHOSPHOMOLYBDATE PRECIPITATE.

By J. R. CAIN AND J. C. HOSTETTER.

Received December 27, 1911.

1. INTRODUCTION.

The fact that vanadium is carried down with ammonium phosphomolybdate when the latter is precipitated in solutions of the former has long been known. Likewise, the fact that the precipitate so obtained has different properties from the normal phosphomolybdate has been mentioned by several authors. The orange to brick-red color of this vanadium-bearing precipitate is quite different from the color of the normal ammonium phosphomolybdate, called from its color the "yellow precipitate." Brearley and Ibbotson[1] mention the increased solubility in dilute nitric acid of the vanadium-bearing precipitate over the normal precipitate, and give some conditions to lessen precipitation of vanadium with phosphorus in steel analysis. The phenomenon has usually been studied with regard to the determination of phosphorus in the presence of vanadium, since the precipitation of vanadium with ammonium phosphomolybdate interferes with an exact determination of phosphorus by the ordinary methods. Especially is this true in steel analysis. The possibility of easily separating vanadium from iron by this method has, we believe, never been studied before. The present research was undertaken in order to decide whether or not vanadium could be completely precipitated with phosphoric acid, and, if so, to learn if it could be determined quantitatively.

2. PRELIMINARY CONDITIONS FOR PRECIPITATING THE VANADIUM.

The necessary ratio of phosphoric acid to vanadic acid for complete precipitation of the latter was investigated qualitatively by following the change in color of the phosphomolybdate precipitated with increasing additions of phosphoric acid. A nitric acid solution of a vanadium-free steel was prepared; to this was added a known amount of vanadium from a carefully standardized ammonium vanadate solution. To equal volumes of the steel solution so prepared were added gradually increasing volumes of a roughly standardized sodium phosphate solution, and the phosphoric acid was precipitated by the molybdate reagent, observing the conditions for this precipitation usually given in texts on steel analysis. With small amounts of phosphoric acid the precipitate was of a deep orange color, which became progressively lighter as the phosphorus increased, finally approaching the color of the normal or vanadium-free phosphomolybdate when relatively very large amounts of phosphoric acid were added. The filtrates were treated by precipitating a further small amount of phosphoric acid, and judging by the color of the precipitate whether or not precipitation was complete the first time. The color of the precipitate proved to be a very delicate qualitative criterion, and very soon it was possible in this manner to fix with fair accuracy the ratio of phosphoric acid to vanadic acid in order to carry down all the vanadium with one precipitation. As methods for the quantitative determination of the vanadium were developed this ratio was determined with greater accuracy. The mechanism of the precipitation and the question of this ratio are subjects that will be described in more detail in another paper. It is sufficient for the present purpose to say there is a co-precipitation of vanadium under the above general conditions, which can be controlled accurately enough to make the precipitation uniformly quantitative. The conditions will be detailed later.

Other questions affecting the probable accuracy of the determination were (1) the solubility of the vanadium-bearing precipitate in the usual washing solutions, and (2) the optimum temperature for precipitation. As to the solubility of the precipitate, it was soon found that the presence of vanadium caused marked changes in the solubility of ammonium phosphomolybdate. It was noticed that when the precipitate dissolved to any extent in the washing solutions these were strongly colored, usually having a straw or orange tint. It was thus possible to decide this question qualitatively, and Table I gives some of the results obtained. It will be seen that acid ammonium sulfate and ammonium nitrate solutions are best adapted for washing the yellow precipitate. Incidentally, the marked solubility in dilute solutions of potassium nitrate and of nitric acid is of interest, for these are the wash solutions recommended by some authorities for use when determining phosphorus in steel. It is evident that such use may occasion errors in the phosphorus determination if vanadium is present in appreciable amount. It seems probable that the solubilities vary considerably with the proportion of vanadium present in the precipitates.

[1] "The Analysis of Steel Works Materials," **1902**, p. 165.

TABLE I.—ORDER OF SOLUBILITY OF VANADIUM-BEARING PRECIPITATE[1] IN VARIOUS SOLVENTS AT ROOM TEMPERATURE.

Solvent.	Concentration.	Color of solution.
Ammonium acid sulfate[2]		Colorless
" nitrate	Saturated solution	"
" "	10 per cent.	"
" sulfate	50 "	Faint yellow
Nitric acid	50 "	Color increases regularly down the series, showing increasing solubility
"	25 "	
Ammonium sulfate	30 "	
" nitrate	1 "	
" chloride	1 "	
" sulfate	10 "	
Sulfuric acid	50 "	
Water		
Ammonium molybdate (neut.)	1 "	
Potassium nitrate	1 "	
" sulfate[3]	1 "	Deep yellow (complete solution).
Nitric acid[3]	1 "	
Sodium sulfate[3]	1 "	
Ammonium molybdate (neut.)[3]	10 "	

The optimum temperature for precipitation in this connection is governed largely by considerations affecting the physical properties of the precipitate and the speed of precipitation. Accordingly, our precipitations are made from solutions brought to boiling before addition of the precipitant, thus securing a rapidly settling precipitate readily filtered by suction. Certain theoretical reasons, to be considered at another time, likewise demand a precipitation at this high temperature. Brearley and Ibbotson[4] also have shown that more vanadium is precipitated at high than at low temperatures.

After having assured ourselves qualitatively that vanadium is completely precipitated by the phosphomolybdate precipitate obtained under proper conditions, a study was made of methods for determining the vanadium thus precipitated.

3. SEPARATING THE VANADIC ACID FROM THE MOLYBDIC ACID.

In view of the easy volatility of molybdic acid, it was at first thought practicable to heat the precipitate over a blast lamp until all the molybdenum had been driven off. It was found that nearly all the molybdenum could be volatilized, but there are too many difficulties encountered to make the method reliable. There is much danger of mechanical loss where the relative amount of vanadium is small; moreover, at the temperature required for rapid volatilization, the vanadium pentoxide remaining behind fuses and creeps over the side of the boat or crucible used as a container, a fact previously noted by Gibbs.[5] Further, there is usually a slight reduction of molybdenum to a lower oxide which does not volatilize readily. However, this method of handling the precipitate has some merits, particularly if one wants visual confirmation of the presence of vanadium in a sample of material. The characteristic appearance of fused vanadium pentoxide is easily distinguished in the residue after ignition, even though some of the lower (blue) oxide of molybdenum is present. Of course, this precipitate can be taken up by fusion with sodium carbonate and precipitated by mercurous nitrate or in any other manner desired. Usually it is accompanied by some iron oxide. We consider that the method is subject to too many irregularities and is too difficult of manipulation for technical work. Moreover, it is much slower than other procedures to be described later. We found that Truchot[1] had also proposed and made use of the volatility of molybdic acid to separate it from small amounts of vanadium coprecipitated with molybdenum, when electrolyzing ammoniacal solutions of molybdates and vanadates.

A very much simpler and shorter method has been devised by us for separating the vanadium in pure form from the phosphomolybdate precipitate. The latter is suspended in a small amount of hot water, and dilute ammonia added drop by drop, with vigorous shaking, until everything is in solution. The solution is heated until all but a trace of ammonia is expelled. The success of the operation depends on the presence of a very small amount of free ammonia at this stage. If too much ammonia is present, the precipitate subsequently obtained on adding mercurous solution carries down some molybdenum. On the other hand, enough ammonia must be present to form a sufficient volume of amido precipitate to bring down the vanadium. One or two trials will enable the operator to decide as to the proper excess. When the right amount of ammonia is present, the solution is filtered, if necessary, and enough mercurous nitrate solution is added to it to give an appreciable acid reaction with litmus paper.[2] Usually a voluminous black precipitate separates on shaking; if it does not form and settle rapidly, the solution is heated until it does. The precipitate is washed by decantation two or three times with water containing 1 per cent. mercurous nitrate, and is finally transferred to the filter and washed there two or three times more. Filter and contents are transferred to a porcelain crucible, the filter paper burned off, and the mercury volatilized. The vanadium remains partly as vanadic pentoxide, partly as lower oxides and is accompanied by relatively very little molybdenum. The latter may be precipitated, if desired, by hydrogen sulfide (after the vanadium has been dissolved out of the crucible with concentrated sulfuric acid and the solution diluted) leaving a pure vanadium solution. If the vanadium pentoxide is dissolved out of the crucible with concentrated sulfuric acid, the intense brown or orange color, characterizing such solutions of vanadium pentoxide is very characteristic; if blue or green tints (due to lower oxides of molybdenum and vanadium) are present, these disappear on the addition of a trace of nitric acid, and evaporation until dense strong fumes appear.

We have not used this method for obtaining quantitative separations of vanadium, although it would probably be successful if the filtrates were treated a second or third time, and the precipitates combined. However, by far the greater portion of the vanadium is obtained at first.

[1] Containing approximately 0 4 per cent. vanadium.

[2] See p. 250.

[3] 0 5 gram of precipitate dissolves in less than 20 cc. of the solvent.

[4] *Loc. cit.*, p. 165.

[5] *Am. Chem. J.*, **5**, 371 (1883–1884).

[1] *Ann. chim. anal.*, **7**, 165–7 (1902).

[2] Caused by the hydrolysis of the mercurous nitrate solution.

The principal use we have made of these methods, as stated above, has been for the purpose of actually isolating the vanadium where there could be the slightest doubt as to its being present at all. In this manner, we believe, the value of the method, from a purely scientific standpoint, is increased. For technical or practical purposes it is never necessary to separate the vanadium from the molybdic and phosphoric acids in order to determine it accurately.

4. REDUCTION OF THE VANADIC ACID BY SULFUR DIOXIDE.

Edgar's method[1] of reduction by sulfur dioxide was next tried, with the idea of reducing the vanadium to the tetravalent stage without affecting the molybdenum; the tetravalent vanadium could then be titrated against permanganate, as usual. Edgar found that by properly adjusting the acidity (sulfuric acid) of his solution and its molybdenum concentration, the differential reduction could be made with ease. Our results are confirmatory, but unfortunately the method is limited in its application to the present problem because of the effect of the presence of iron occluded by the large amount of ammonium phosphomolybdate sometimes required. This iron is sometimes present in relatively large quantities and of course is wholly or in part reduced by the sulfur dioxide. It is difficult, too, to completely eliminate this impurity from the precipitate without unduly prolonging the process. Solution of the precipitate, followed by reprecipitation, helps but little. If the precipitate is dissolved in ammonia, a clear solution is obtained, even if considerable iron is present; the latter reveals its presence by imparting a dark color to the otherwise colorless solution. If, however, the precipitate is dissolved in sodium hydroxide, a large proportion of the iron separates and the precipitation can be made nearly complete by boiling the solution until all the ammonia of constitution of the yellow precipitate is expelled.

We made a number of fairly accurate determinations of vanadium in the presence of iron and chromium by precipitating the vanadium with phosphomolybdate, dissolving the precipitate in ammonia, acidifying with sulfuric acid to a 15 per cent. acidity, followed by sulfur dioxide reduction and permanganate titration. In most of the determinations it was necessary to get rid of the iron contaminating the phosphomolybdate by dissolving the latter in sodium hydroxide solution and filtering off the ferric hydroxide, as above. It was found that chromium in the trivalent condition did not affect the determination of vanadium at all.

A series of determinations by this method now gave the necessary data for accurately fixing the ratio of phosphorus to vanadium to secure complete precipitation. It was established that ten times as much phosphorus as there is vanadium to be determined would insure complete precipitation of all the vanadium and allow a sufficient margin of safety for variation from suspected composition. We have used this ratio in all subsequent determinations. Of course, where the vanadium content of a sample is not known within sufficiently close limits, it is necessary to make two or more phosphomolybdate precipitations, testing each for vanadium. However, this is about what one has to do with any method when working on unknown materials.

The method of reducing the vanadium by sulfur dioxide and titrating against permanganate having proved, in our opinion, too long and uncertain for technical use, other methods were tried.

5. COLORIMETRIC DETERMINATION OF THE VANADIC ACID.

Gregory's colorimetric method,[1] depending on the colors developed in strong sulfuric acid solutions of vanadium and strychnine, seemed promising, inasmuch as the phosphomolybdate is so soluble in concentrated sulfuric acid. We found by preliminary tests that the associated molybdenum has no appreciable effect on the strychnine, so far as color development is concerned. However, iron does, and this is to be expected from Allen's statement of the cause of the color:[2] "On treating a cold solution of strychnine in concentrated sulfuric acid with an oxidizing agent of almost any kind a rich purple-blue coloration is developed. This changes more or less rapidly through purple and crimson to a bright cherry-red tint, which is somewhat persistent." From this it was evident that ferric iron must be absent and probable that the vanadium must be in the pentavalent state. We confirmed the latter by trials of concentrated sulfuric acid solutions of V_2O_4, which gave no color with strychnine. This is an important point, for we found that strong sulfuric acid solutions of vanadium pentoxide are very prone to go over to the quadrivalent state, when of course they develop no color with strychnine. With sulfuric acid solutions of the phosphomolybdate precipitate containing vanadium it is easy to follow this change by the change of color in the solution. Initially there is a straw or orange color,[3] apparently due to the presence of acid vanadates or polyacids,[4] which is probably closely proportional to the amount of vanadium present, but after a few minutes' evaporation to strong sulfur trioxide fumes, and with low vanadium content, the solution becomes either colorless or a pale blue. We observed the same phenomenon with concentrated sulfuric acid solutions of vanadium pentoxide. At first the reduction was thought to be due to organic matter present in the sulfuric acid, but further experiments with larger amounts of vanadium showed too much reduction to be accounted for in this way. For instance, in one experiment 8 mg. of vanadium as pentoxide dissolved in 15–20 cc. of sulfuric acid were fumed in a carefully covered flask for four or five hours, at the end of which time

[1] *Am. J. Sci.*, [4] **25**, 332 (1908). See also Gibbs: *Loc. cit.*

[1] *Chem. News*, **100**, 221.

[2] "Commercial Organic Analysis," Vol. III, 2nd Ed., Pt. II, p. 368.

[3] Some work has been done here toward making this color the basis of a colorimetric method for vanadium.

[4] Gmelin-Kraut, "Handb. d. Anorg. Ch.," 7th Auf., Vol. III, Pt. 2, p. 89.

reduction was practically complete. We found that Prandtl[1] had already investigated this matter and concluded that under these conditions there is a dissociation of the vanadium pentoxide in analogy to the behavior of chromic anhydride dissolved in concentrated sulfuric acid. This behavior was the opposite of what we had expected, after having read the work of Koppel and Behrendt,[2] who found the reverse action taking place. Possibly there is an equilibrium between the two sets of reactions. This complication is very troublesome when attempting to prepare the sulfuric acid solution of the vanadium-bearing phosphomolybdate for colorimetric estimation by strychnine. As stated above, with small amounts of vanadium (for which we had expected the colorimetric method to be very useful), the reduction or dissociation takes place completely in a few minutes after the precipitate is dissolved in sulfuric acid. Such a solution treated at once with strychnine either gives no color, or a much less intense color than corresponds to the actual amount of vanadium present. On the other hand, if the attempt is made to reoxidize the vanadium to the pentavalent stage, this must be accomplished under difficult conditions, for no excess of the oxidizer must be left in the solution (inasmuch as this would give a color with the strychnine), nor must the solution be heated unduly long in attempting, for instance, to destroy or drive off the excess of oxidizer, for as soon as the excess disappears the vanadium goes quickly to the quadrivalent stage. Thus, while it was easy to oxidize the vanadium with a minute quantity of nitric acid, we could never be sure that the excess had been driven off and at the same time no vanadium had been reduced. We attempted to find an oxidizing agent that would oxidize the vanadium without affecting the strychnine and found that bismuthate would do so under very special sets of conditions, but there were complications attending its use, such as clouding of solutions in the colorimeter, occasional unexplained development of color in blanks, etc., that led us to abandon its use altogether. Besides the uncertainties and complications occasioned by solution in concentrated sulfuric acid already mentioned, which necessitate oxidation with reagents liable to cause high results if used (or low ones if not used), and those arising from the presence of iron with the phosphomolybdate, necessitating reprecipitation, there is also the possible accidental introduction of organic matter at various stages where reduction of vanadium might occur, and the troublesome manipulation of concentrated sulfuric acid in the colorimeter. The colorimetric method of determining vanadium in the precipitate at first appealed to us because of its apparent simplicity and wide range of application, but the results of an extended series of determinations lead us, for the present, at least, to abandon these views.

5. REDUCTION OF THE VANADIUM BY HYDROGEN PEROXIDE

(*a*) *General.*—In attempting to find a suitable oxidizer for preparing the vanadium solutions for colorimetric determination, we tried hydrogen peroxide, and were thus led to the discovery of the reaction which is made the basis of the method we have finally adopted for determining vanadium in the phosphomolybdate precipitates. Much to our surprise, the peroxide, used in concentrated sulfuric acid solutions, acted as a reducing instead of an oxidizing agent, so that by its use we were able to easily reduce the vanadium quantitatively to the tetravalent stage. Moreover, we found by careful tests that the associated iron and molybdenum were never affected. We found that solid peroxides could also be used, but hydrogen peroxide is to be preferred, in general. The details of the reaction will be given fully in another paper and stated here only in so far as they apply to the method of analysis. To carry out the reduction, all that is necessary is to dissolve the phosphomolybdate-vanadium precipitate in concentrated sulfuric acid (filtration having been made on asbestos), add a few drops of nitric acid, fume strongly for two or three minutes, remove from the hot plate, allow to cool, and add hydrogen peroxide in very small quantities, with vigorous shaking after each addition, until the solution takes on a deep brown color (due to action on the molybdate); this always disappears on heating, and is followed by the clear green or blue color (depending on the ratio of V to Mo) of vanadyl vanadium. The flask is replaced on the hot plate and the solution fumed for a few minutes, after which it is cooled, diluted and titrated against permanganate. The whole operation is extremely simple, the end-point very good, and as our data show, the results are very accurate.

(*b*) *The Method.*—For steels containing vanadium, chromium, nickel, titanium, manganese, molybdenum, singly or in combination, dissolve an amount of drillings estimated to contain 2 to 10 mg. of vanadium in nitric acid (sp. gr. 1.135), boil till free from fumes, oxidize with permanganate solution, dissolve the manganese peroxide in sodium sulfite solution, and boil till free from fumes. In other words, prepare the solution exactly as for a phosphorus determination, examining any insoluble for vanadium. Nearly neutralize with ammonium hydroxide (0.96) and add an amount of sodium phosphate solution containing at least ten times as much phosphorus as there is vanadium present. Bring the solution to boiling, remove from the plate and add at once the usual necessary excess of the molybdate reagent to precipitate the amount of phosphoric acid added. Agitate for a minute or so, when it will be found that the precipitate settles rapidly. Filter the supernatant liquid by suction through an asbestos filter, and wash three times by decantation with hot acid ammonium sulfate solution, pouring the washing liquid through the filter. The last wash solution should be decanted off as completely as possible from the precipitate in the flask and the filter should be sucked dry. The rubber stopper carrying the filter is now fitted to a small, dry bottle, and hot, concentrated sulfuric acid is poured on the filter to dissolve the small amount

[1] Gmelin-Kraut, "Handb. d. anorg. Ch.," 7th Auf., Vol. III, Pt. 2, p. 87.
[2] *Zischr. anorg. Chem.*, **35**, 156 (1903).

of precipitate thereon. This dissolves quickly and the solution is drawn through by suction into the bottle. The contents of the bottle are transferred to the flask in which precipitation was made, and the bottle is washed once with concentrated sulfuric acid, the washings being added to the flask. For every 10 mg. of phosphorus present a final volume of 5 to 8 cc. of concentrated sulfuric acid is necessary. The contents of the flask are heated until solution takes place, a few drops of nitric acid (1:25) added and, when fumes are coming off strongly, the flask is removed from the plate and the vanadium reduced by successive small additions of hydrogen peroxide as above described. Replace on the hot plate, fume for four or five minutes, cover the flask, cool, dilute so as to secure an acidity of one part to five by volume, and titrate at a temperature of 70° to 80° C. against 0.01 N permanganate. The condition as to acidity and temperature must be closely observed in order to secure a satisfactory end-point.

For steels of the above classes containing tungsten, the only change necessary is to dissolve in aqua regia, dilute with hot water, filter off the tungstic acid, nearly neutralize with ammonium hydroxide, and add 10 grams solid ammonium nitrate for every 100 cc. of the final volume[1] before precipitating as above described. If desired, the tungstic acid on the filter may be dissolved in a small amount of sodium hydroxide solution (free from vanadium), acidified with nitric acid and tested for vanadium by hydrogen peroxide. We have not found vanadium here, and accordingly make no provision for its determination.

(*c*) *Solutions Necessary.*—Nitric acid of sp. gr. 1.135. Use 20–25 cc. for each gram of drillings to be dissolved.

Potassium permanganate for oxidations: 15 grams per liter.

Sodium sulfite: 50 grams per liter. A solution of sulfurous acid may be substituted.

Sodium phosphate: 124 grams $Na_2HPO_4.12H_2O$ per liter. One cc. contains approximately 10 mg. of phosphorus and will precipitate 1 mg. of vanadium. The solution may be standardized by evaporating a definite volume to dryness, igniting the residue and weighing the $Na_4P_2O_7$ so formed.[2]

Molybdate reagent: Make up according to the usual formula; 1 cc. will contain 0.05 to 0.06 gram MoO_3. For every mg. of phosphorus to be precipitated use at least 2 cc. of molybdate reagent. This ratio is used, however, only when precipitating large amounts of phosphorus. When precipitating small quantities of phosphorus 50 cc. of molybdate solution is the minimum volume used.

Acid ammonium sulfate: To 1000 cc. of water add 15 cc. ammonium hydroxide (0.90) and 25 cc. of sulfuric acid (1.84).[3] Use at a temperature of 80° C.

Potassium permanganate, 0.01 *N:* Standardize against sodium oxalate,[4] or, empirically, against a steel in which the vanadium has been accurately determined by other methods.

Peroxide: Hydrogen peroxide, 3 per cent. We have made our reagent with "Perhydrol." "Di-oxygen" also proved satisfactory.

Table II shows a few of the very large number (in all nearly 400) of determinations made by us to be sure that the method is reliable. Nos. 16 and 17 of Table II are of interest as showing the delicacy of the method. As a matter of fact the vanadium can just as easily be concentrated from 50 or even 100 grams of steel or iron, so that excessively small per-

TABLE II.—RESULTS OBTAINED BY THE PEROXIDE REDUCTION METHOD.[1]

No.	Amount of sample. Grams.	Cr present. Mg.	P added. Mg.	V present. Mg.	V found. Mg.	V_2O_5 found. Per cent.
1	1	45	12	1.11	1.17	
2	1	180	20	1.92	1.91	
3	1	135	35	3.19	3.26	
4	1	90	45	4.52	4.60	
5	1	45	60	6.38	6.49	
6	1	225	100	10.64	10.73	
7	1	50	10	1.02	1.16	
8	1	100	25	2.54	2.58	
9	1	150	40	4.06	4.15	
10	1	200	50	5.08	5.07	
11	1	250	60	6.08	6.18	
12	1	50	80	8.13	8.40	
13	1	100	90	9.12	9.42	
14	1	150	100	10.15	10.22	
15[2]	5		19		0.995	
16	20		20	1.00	1.02	
17	20		19	1.11	1.24	
18	1		25	2.66	2.75	
19	2		19		1.07	0.078
20	10		39		3.41	0.05
21	10		19		0.66	0.01
22	10		19		0.81	0.012

centages can be detected and determined with ease. Nos. 19, 20, 21 and 22 of the same table show the application to other materials, the results on the titaniferous magnetite ore being of special interest.

If the expected content of vanadium in a sample is not known accurately enough for adding the necessary excess of phosphoric acid, two or more precipitations may be necessary.

We have found the arrangement shown in Fig. 1 useful for handling the concentrated sulfuric acid; it is much more convenient to use than a reagent bottle. It stands on a large sheet of glass. Also, the funnel with glass stopper shown in Fig. 2 is useful but not necessary. It is made by sealing a carbon filter to the inlet tube of a thick-walled glass wash-bottle, the latter being used as a suction filter flask.

[1] Except as otherwise indicated, the solutions used for these determinations were made by adding chromium and vanadium to the nitric acid solution of a vanadium and chromium-free steel in the proportions indicated in the table. The vanadium was added from an ammonium vanadate solution, which was standardized by reducing with sulfur dioxide and titrating against permanganate; the chromium was added from a chrome-alum solution, the chromium content being calculated from the amount of salt weighed out.

Nos. 1 to 6, and 15 to 22, inclusive, reduced with magnesium peroxide.

Nos. 7 to 14, inclusive, reduced with hydrogen peroxide.

[2] No. 15, B. S. Chrome-tungsten Steel Standard No. 30 (in preparation). (V found = 0.02 per cent.; not determined by any other method.)

No. 18 contained 23 mg. of titanium as titanium sulfate.

No. 19, B. S. Magnetite Ore Standard, No. 29.

No. 20, B. S. Manganese Ore Standard, No. 25.

No. 21, B. S. Sibley Ore Standard, No. 27.

No. 22, B. S. Crescent Ore Standard, No. 26.

[1] Bureau of Chemistry, *Bull.* **107** (Revised), p. 3.

[2] Baxter, *Am. Chem. J.*, **28**, p. 301 (1902).

[3] Blair, "The Chemical Analysis of Iron," 7th Ed., p. 97.

[4] Bur. Stand., *Circular* **26**, 2nd Ed., p. 10.

If rubber stoppers are used, they should be good sound ones, so that pieces of rubber cannot drop into the concentrated sulfuric acid solutions.

The largest amount of vanadium determined in Table V (10 mg., or 1 per cent. on a one-gram sample) gives about as large a volume of precipitate as it is convenient to handle. We have precipitated and determined accurately as much as 27 mg. of vanadium, using the 10 to 1 ratio of phosphorus, but the manipulation in such cases becomes inconvenient. This is about the only serious limitation placed on the method, making it necessary, when dealing with large amounts of vanadium, to precipitate from an aliquot corresponding to a relatively small sample. For steels, alloys, ores, rocks, etc., containing from

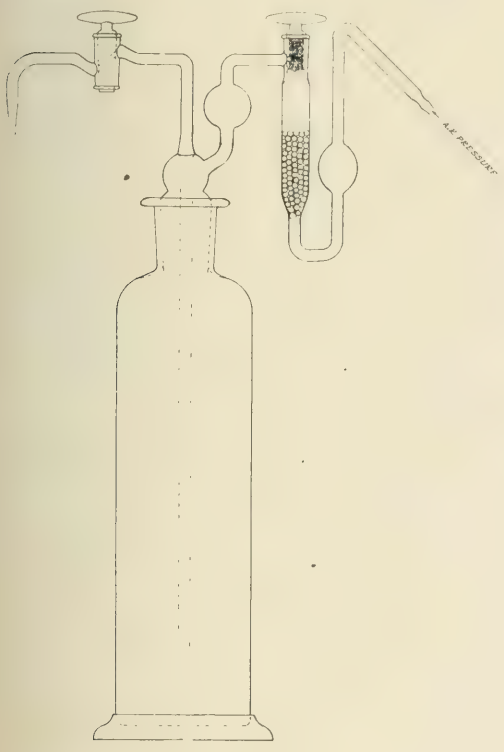

FIG. 1.

traces up to 5 or 6 per cent. of vanadium the method, we believe, can be used wherever phosphorus can be precipitated as phosphomolybdate from solutions of these materials.

7. NOTES AND PRECAUTIONS.

The presence of vanadium in the phosphomolybdate precipitate is shown by the yellow to orange color of the cold, concentrated sulfuric acid solution of the precipitate, 0.05 mg. vanadium showing a perceptible color in a volume of 25 cc.

In carrying out the peroxide reductions it is necessary to use a flask instead of an open dish or beaker. If the latter is used there is reduction of the molybdenum where the strong solution acid "creeps" up along the sides of the vessel, the reduction showing by the development of an intense blue coloration.

If, after the addition of peroxide and subsequent heating, the vanadium is not reduced, it is probably due to traces of nitric acid in the solution, which may be removed by further fuming; the treatment with peroxide should then be repeated. In this connection we may note that nitrous fumes readily oxidize tetravalent vanadium and hence the reductions should be carried out in an atmosphere free from such fumes. After the reduction, it is advisable to cover the flask with a watch glass while the solution is cooling in order to prevent accidental introduction of organic matter.

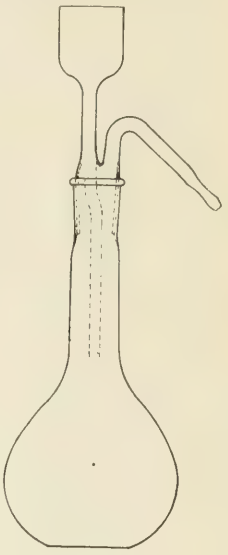

FIG. 2.

If the final titration is carried out in acid of greater concentration than 1–2 by volume, the end-point is rendered uncertain because of the deep yellow color which the pentavalent vanadium, formed during the titration, gives with strong sulfuric acid. We recommend a dilution of 1–5, in which the end-point is very sharp.

The time required for making a determination is worthy of note. Working with a vanadium steel, the sample was weighed out, dissolved and precipitated in 10 minutes, the precipitate washed and dissolved in sulfuric acid in 9 minutes more, while the reduction and titration required a further 12 minutes, giving the completed determination in approximately $^1/_2$ hour. By operating on a large number of samples at one time, the determination can be made as rapid, if not more so, than that of phosphorus in steels. We have frequently completed 20 determinations in less than 7 hours, even while giving much attention to uncompleted details. With these worked out, the method should allow the completion of twice as many determinations in a day.

Manganese ores are readily decomposed with hydrogen peroxide in the presence of nitric acid. This solution is very well adapted for the determination of vanadium; the insoluble should also be tested.

When precipitating vanadium from a solution containing hydrochloric acid and, in general, when the volume of the solution is very great we recommend the addition of 10 grams of solid ammonium nitrate for every 100 cc. of solution.

8. SUMMARY.

(1) It was found that vanadic acid may be quantitatively precipitated by ammonium phosphomolybdate.

(2) The vanadium-bearing phosphomolybdate shows

different solubility relations compared with the normal phosphomolybdate, with respect to the usual washing solutions used in determining phosphorus.

(3) Conditions are given for quantitatively precipitating vanadic acid when in solution alone, or accompanied by a variety of other elements, by means of ammonium phosphomolybdate.

(4) In order to determine quantitatively the vanadic acid so precipitated, (*a*) the possibility of freeing it from the accompanying molybdic acid was investigated.

(*b*) Conditions for reducing it without reducing the associated molybdic acid were developed.

(*c*) A method for reducing it by hydrogen, and other peroxides and titrating it against permanganate was elaborated.

(5) The method (*c*) was applied to a variety of steels, to iron ores, manganese ores, and to synthetic mixtures, in all of which the vanadium was determined with great accuracy.

BUREAU OF STANDARDS,
WASHINGTON, D. C.

A NEW METHOD FOR THE DETERMINATION OF VANADIUM; AN EXPLANATION.

By J. R. CAIN AND D. J. DEMOREST.

Received January 25, 1912.

The discrepancy in results obtained by us when using manganese dioxide, as mentioned in the paper on "A New Method for the Determination of Vanadium," page 249, led us to seek the cause. We exchanged samples of manganese dioxide and each found that the other's reagent behaved as stated in our respective papers. However, it was noted by Mr. Cain that Mr. Demorest's dioxide, which oxidized differentially, was much coarser than the manganese dioxide which the former had used, and which oxidized both the lower oxides of vanadium and iron. Upon grinding the coarse manganese dioxide very fine he found that it oxidized both iron and vanadium oxides as his own preparation had done. On the other hand, Mr. Demorest succeeded in separating a coarse portion from the manganese dioxide used by Mr. Cain which oxidized differentially.

Thus, the discrepancy is evidently due to a difference, in the two cases, of the velocities of the reactions:

$$(1)\ V_2O_4 + MnO_2 = MnO + V_2O_5$$
$$(2)\ FeO + MnO_2 = Fe_2O_3 + MnO$$

Mr. Demorest's reagent had a degree of fineness such that in the brief period of treatment the velocity of reaction (1) was inappreciable and reaction (2) was completed; whereas with material of the fineness used by Mr. Cain both reactions went to completion. The securing of such different results merely by changing the size of the grain of the reacting solid seems a matter worthy of further investigation.

THE RAPID DETERMINATION OF VANADIUM IN STEEL.

By FRANK GARRATT.

Received Dec. 20, 1911.

The writer has for some time used the following modification of Johnson's method[1] for determining vanadium in steel. Johnson's procedure is adhered to in all respects, except that the oxidation of the chromium and vanadium in hot, dilute sulfuric acid with potassium permanganate is omitted. With this omission the method is extremely simple and, briefly, is as follows:

Dissolve 2 grams of steel in about 50 cc. of dilute sulfuric acid; when solution is complete, oxidize the iron, and tungsten if present, by adding about 5 cc. of concentrated nitric acid to the hot solution. Boil until nitrous fumes are expelled, or in the case of tungsten steels, until the separated tungstic acid is of a pure yellow color. Dilute the solution to about 150 cc., filter if tungstic acid is present, and cool to room temperature. Dilute to about 350 cc. in a suitable beaker, add a little ferrous sulfate solution, and obtain the old rose shade with permanganate. Add the potassium ferricyanide indicator, and titrate at once with standard ferrous ammonium sulfate solution for the vanadium value.

As pointed out by Johnson, blanks must be run on steels of similar composition, and consistent endpoints adhered to in the titrations. As outlined above, the determination, even in the case of tungsten steels, may be completed in 20 minutes. If tungsten is absent the filtration may, of course, be omitted, thus shortening the operation.

If chromium is not to be determined, there is no reason, of course, for its oxidation. As a matter of fact, without this oxidation the blanks seem to be smaller and more uniform. Carbonaceous matter does not seem to interfere in the subsequent titration.

The writer thinks that Johnson's scheme of adding the ferricyanide indicator to the solution to be titrated, gives the most practical method yet offered for the technical determination of vanadium in steel. Blair's method,[2] with proper precautions, leaves nothing to be desired in the way of accuracy, but it consumes too much time and care for a busy works laboratory. Cain's method[3] is, of course, much shorter but it does not offer the advantages in regard to simplicity and rapidity that Johnson's method possesses. Blair's and Cain's methods may well be considered desirable for standardizations and umpire determinations, but Johnson's method seems to be *the* one for routine work. If the procedure described herewith is adopted, the determination of vanadium is much simplified, and takes its place with the rapid methods for determining carbon, phosphorus, manganese, etc. Certainly the laboratory doing routine work on vanadium steels need not worry about its determination.

The following table gives some results obtained by this rapid modification. Some of the steels contained no chromium, while others varied from 0.90–6.00 per cent. The presence of chromium offers

[1] "Chemical Analysis of Special Steels, etc.," p. 8.
[2] *J. Am. Chem. Soc.*, **30**, 1229.
[3] THIS JOURNAL, **3**, 476.

no complications, however, simply increasing the blank to be deducted from the ferrous ammonium sulfate used in the final titration.

No.	Per cent. V. By Blair's method.	Added as NH_4VO_3.	Per cent. V by rapid method	Difference by rapid method.
1	0.14	....	0.15	+0.01
2	0.25	....	0.25	none
3	0.47	....	0.45	—0.02
4	0.64	....	0.65	+0.01
5	0.89	....	0.88	—0.01
6	1.13	....	1.13	none
7	1.27	....	1.29	+0.02
8	1.31	....	1.31	none
9	1.37	....	1.37	none
10	4.67	....	4.68	+0.01
11	....	0.15	0.16	+0.01
12	....	0.50	0.50	none
13	....	1.00	0.99	—0.01
14	....	1.00	0.98	—0.02

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THE DIRECT DETERMINATION OF SMALL AMOUNTS OF PLATINUM IN ORES AND BULLION.[1]

By FREDERIC P. DEWEY.

By the old method of determining platinum in ores and bullion, the silver-alloy first obtained in the regular course of assay is parted in strong sulphuric acid and the residual metal weighed. This is realloyed with silver by a second cupellation and parted in nitric acid, the residual metal being again weighed. Any difference shown between the two weighings is assumed to be, and is called, platinum. Sometimes it is so, and if any considerable amount of platinum be present, there will be a decided difference between the two weighings; but a slight difference is no real evidence whatever of the presence of platinum. On the other hand, the second weight may equal or possibly exceed the first, even when traces of platinum are present. Again, other members of the platinum group may go into solution in nitric acid more or less. If present, these would be called platinum and escape detection. The method does not provide any direct tests whatever as to the presence or absence of platinum. It is often indecisive and sometimes gives erroneous results. It is, therefore, quite unsatisfactory.

Being called upon many times to determine platinum, in a wide variety of materials, particularly when present in very small amounts, I have realized the disadvantages and defects of this old method.

In an article on the solubility of gold in nitric acid,[2] I have briefly outlined a method of gathering a little gold out of a solution containing much silver, which furnishes the basis of an excellent method for the direct and absolute determination of small amounts of platinum and has the added advantage that the metal weighed may be subjected to suitable tests, to determine that it really is platinum, and to reveal the presence of other members of the platinum group.

In the regular course of assaying for the precious metals, gold is parted from silver by dissolving the silver in nitric acid. If platinum be present in small amounts only, it will readily go into solution in the nitric acid. If now a limited amount of hydrogen sulphide be added to the solution from parting, any platinum present will be precipitated as sulphide, along with some silver sulphide. On filtering off the precipitate (which generally is sufficiently washed by the operations necessary to transfer it from the precipitating dish to the filter), the moist filter is transferred to a small porcelain crucible, dried at a low heat, and burned off by gentle ignition. This transforms the sulphide precipitate into a metallic sponge, which is wrapped in a small piece of thin lead foil and cupelled. The resulting bead is then parted in strong sulphuric acid, when the platinum will be left as a dark residue, generally collected in spongy form, even when minute in quantity. This sponge, after reboiling in fresh acid, if necessary, is suitably washed by decantation, annealed, and weighed.

Generally, the final metal speaks for itself as being platinum, but, if there should be any doubt, it may be dissolved in a drop or two of aqua regia and gently evaporated. The solution obtained may be tested with potassium iodide, or a few small crystals of ammonium chloride may be added, when the characteristic precipitate will show itself. As a further test this may be filtered off and gently ignited to produce spongy platinum. If the amount of the final metal be considerable, the platinum may be determined by the double-chloride method. Any decided difference shown would indicate the presence of other members of the platinum group, for which direct test could then be made.

For precipitating the platinum and the necessary silver from the parting-solution, a very dilute solution of hydrogen sulphide should be used. One part of a strong solution should be diluted to from 10–20 parts with water. If the solution of silver nitrate be strongly acid, it should be largely diluted, or it may first be evaporated and then diluted. The very dilute hydrogen sulphide solution should be added very slowly to the silver nitrate solution with constant stirring. The solution is, of course, at once darkened, but there should be no immediate separation of a visible precipitate. The solution should be stirred occasionally, and in about 2 hrs. flocks of precipitate should appear. It may be filtered in from 3–4 hrs., but it is a good plan to let it stand over night if possible.

The amount of hydrogen sulphide required depends, of course, upon the amount of platinum present. If this should be roughly known or suspected, the amount used should generally be enough to precipitate the platinum and from three to five times as much silver. On an entirely unknown ore, I should at first use 1 cc. of strong hydrogen sulphide solution diluted to 15 cc., and reserve the filtrate from the sulphides for retreatment, if necessary. On an unknown bullion

[1] Presented at the New York meeting of the American Institute of Mining Engineers, February, 1912, and published in the Bulletin of the American Institute of Mining Engineers, April, 1912, Serial No. 64.

[2] *J. Am. Chem. Soc.*, **31**, 323 (1910).

I should use 2 cc. of strong solution diluted to 30 cc., partly because bullions are liable to carry much more platinum than any ordinary ore, and partly because the volume of the silver nitrate solution from parting the gold must necessarily be larger. If, however, it is known that minute amounts of platinum are present, it is still necessary to use sufficient hydrogen sulphide to give a silver bead large enough to handle comfortably. For this reason I seldom use less than the equivalent of 1 cc. of strong hydrogen sulphide solution.

It may happen that the final metal shows the yellow color of gold, due to the fact that exceedingly fine float-gold passed over in decanting the solution of silver nitrate from the gold. In such a case the metal must be realloyed with silver and the treatment repeated. When the proportion of gold to silver in the metal being parted is so small that the gold separates in a very finely divided state, it will often save trouble to filter the silver-nitrate solution, to separate any float-gold, before adding the hydrogen sulphide.

This method has been used with the utmost satisfaction in determining very minute amounts of platinum in various silver-products directly. Much of our silver coinage, for instance, will show a few tenths of a milligram of platinum in 100 g. of coin. Recently I examined samples from two purchases of fine silver. Very large samples were dissolved in nitric acid. The acid in portions was poured upon the samples and allowed to act at a gentle heat until exhausted. Finally, a small amount of residual silver was removed from the solution and dissolved in a small amount of fresh acid, the solution being then united with the main solution, and the whole evaporated nearly to dryness. It was then diluted to about 250 cc. and 5 cc. of strong hydrogen sulphide solution diluted to 50 cc. was poured in with constant stirring.

This operation concentrated the gold and platinum of the silver into a small amount of sulphide precipitate. This precipitate was filtered off, roasted, and cupelled. The resulting bead was parted in nitric acid, and the gold determined. The silver nitrate solution was treated with dilute hydrogen sulphide solution, equivalent to about 1 cc. of strong solution, and the platinum parted from the silver by strong sulphuric acid.

These two samples yielded the following results:

No.	Silver taken. Gram.	Gold found. Milligram.	Platinum found. Milligram.
1.....	122.32	0.28	0.67
2.....	125.47	0.12	0.18

In case we have a material containing a considerable amount of platinum, the well known fact that platinum alloyed with silver is not entirely soluble in nitric acid must be considered. In such a case the gold from the first parting in nitric acid must be alloyed with silver and parted in nitric acid a second, or even a third time, before proceeding to precipitate the platinum from the parting solutions with hydrogen sulphide.

It is also very satisfactory to use the general method of gathering gold in a precipitate of silver sulphide in determining minute quantities of gold in high-grade silver, such as that produced by electrolytic refining. It is comparatively easy to gather the gold from very large samples of silver, up to 100 g. or more, into a decigram of silver, and then part by nitric acid as usual.

Probably this method of precipitating a noble metal in solution, or removing it from suspension in a liquid, by adding hydrogen sulphide in the presence of silver in the solution, could be used to advantage in determining gold in metallic copper and similar materials.

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THE DETERMINATION OF MOISTURE IN COALS.

By E. H. ARCHIBALD AND J. N. LAWRENCE.

Received Feb. 7, 1912.

According to the official method for the determination of moisture in coal, the sample should be heated for one hour, preferably in a double-walled toluene bath, at a temperature of 104–7°, the loss in weight of the sample being taken as the moisture. It is of course recognized by many that the result does not necessarily represent the true moisture, but the magnitude of the error that may be made by following these directions does not seem to be appreciated. The following experiments were undertaken for the purpose of comparing the quantity of moisture which might be found according to the official method, with that which may be taken as representing the true moisture and thus ascertaining the magnitude of the errors which might be caused by oxidation of the coal, and evolution of gases at different temperatures, and the retention of the moisture by certain coals, which, being very porous, hold the water very tenaciously.

The work that has been done upon occluded gases in coal has a direct bearing upon this problem. Obviously, the more gas given off during heating, other things being equal, the larger the error which will be made. That carbon dioxide, oxygen, methane, nitrogen, carbon monoxide and ethane are evolved from peats and coals when heated, has been shown by Websky,[1] VonMeyer,[2] Thomas,[3] and a number of other investigators.

Parr and Baker[4] have shown that when coal is first mined it evolves hydrocarbons, chiefly methane, quite rapidly; but after a period of four months scarcely any methane is given off. Their data also show that carbon dioxide is evolved especially at a high temperature, and that oxygen is continually absorbed.

Porter and Ovitz[5] found that some coals dried in the air at 115° C. lose appreciable amounts of carbon

[1] *J. prakt. Chem.*, **92**, 76 (1864).
[2] *Ibid.*, **5**, 144 (1872).
[3] *J. Chem. Soc.*, **13**, 793 (1875).
[4] *Univ. of Ill. Eng. Exp. Station, Bull.* **32**.
[5] *J. Am. Chem. Soc.*, **30**, 1486 (1908).

lioxide, and a great many take up oxygen. These uthors have also shown that the coal absorbs oxygen vithout forming carbon dioxide.

E. E. Somermeier[1] has called attention to the act that lignitic coals give up their moisture more lowly than harder coals.

Kent[2] has suggested heating the coal in an atmos-here of nitrogen, absorbing the moisture given off by means of calcium chloride, and determining the ncrease in weight of this drying agent, which should epresent the true moisture.

N. W. Lord[3] notes that when finely ground samples f Illinois and Indiana coals were heated for different engths of time, in different amounts, and under lifferent conditions, practically all the moisture was xpelled in the first thirty minutes; further that the hange in weight represented not only the loss of noisture, but included any change due to oxidation, r other cause.

The recent work done by Porter and Ovitz[4] dealing vith the subject in hand is most interesting. They vere especially concerned with the volatile matter volved from the coal at temperatures between 400° nd 1100°. They also conducted a series of experi-nents for the purpose of weighing directly the mois-ure driven off from the coal at 105° when heated in current of dry air or in nitrogen. The gaseous roducts were as far as possible collected and weighed. heir results show that a slight amount of carbon lioxide is produced by drying the Illinois and Wy-oming coals at 105°, but only slight traces of hydro-arbons or carbon monoxide. Their experiments urther showed that oxidation of the coal occurred o the extent of 0.4–0.5%, the amount of moisture btained by absorptions in calcium chloride being reater, in almost every case, than the moisture letermined by the official method.

The particular purpose of our work was to show he effects of heating the coal at different tempera-ures, for different lengths of time, and the extent o which a soft coal must be heated in order to expel he moisture. As will be shown below, the greatest rror made in the determination of the moisture, y the official method, is likely to be due, not to xidation or evolution of gases, but to the different ates at which moisture is expelled from different oals.

In the first set of experiments the coal was placed n a tube and heated in a stream of air free from noisture and carbon dioxide. After passing over he coal, this stream of air was led to tubes containing nhydrous calcium chloride.

The attempt was made to determine the amount f hydrocarbons given off, but this was not entirely uccessful. We can say, however, that the amount s exceedingly small below 110°; there seemed to be ppreciable amounts at 120°.

After heating for an hour, or two hours, the tube ontaining the coal was weighed, giving the change in weight of the coal. Also, the calcium chloride tube was weighed giving the moisture driven out of the coal. The difference between the latter value and the gain or loss in the weight of the coal tube should give the value of the change due to oxidation, evolution of gases and such causes.

If gas was evolved along with the expelled water and some constituent of the coal oxidized at the same time, the change in weight will be negative or positive as the first two effects or the latter are the greater.

In making the weighings, glass tares were used, of very nearly the same volume and surface area, and containing the same amount of substance as the tubes to be weighed. The weights were carefully compared among themselves, and all corrections applied. The balance used was a long arm Becker which gave very constant results.

Blank tests were run frequently in order to assure ourselves that the air or nitrogen used was free from moisture, carbon dioxide, oxygen or any harmful impurity. These tests always gave very satisfactory results.

The experimental work may be classified as follows:

(1) The experiments with bituminous coal heated in a current of air.

(2) The experiments with bituminous coal heated in a current of nitrogen.

(3) The experiments with anthracite heated in a current of air.

(4) The experiments with anthracite heated in a current of nitrogen.

In the case of the first set of experiments the coal was heated at four different temperatures, *viz.*, 75°, 100°, 110°, and 120° starting with a fresh sample of coal for each temperature. Each sample was heated one hour, then weighed, heated two hours and again weighed; while in the case of a few samples the heating was continued for two hours and then for one hour. At each of these intervals the change in weight of the coal and the true moisture given off was determined, as well as the unsaturated hydrocarbons evolved, if any. The data obtained are shown in Table I, expressed as percentages of the original weight of the coal. A gain in weight is indicated by the letter G. A loss in weight by L. These letters are inserted only when the result is different from that indicated by the heading of the column.

The results show that at 75° the loss in weight of the coal corresponds very closely to the moisture expelled from the coal; that an appreciable amount of moisture remained in the coal after the first hour of heating; that practically no unsaturated hydrocarbons were detected.

At 100° the moisture weighed was 0.19% greater than the loss in weight of the coal during the first hour. The coal gained instead of losing in weight during the second and third hours. This shows considerable oxidation as it is enough to cause not only this increase in weight but to make up for the loss due to the evolution of any gases, which must have

[1] *J. Am. Chem. Soc.*, **28**, 1630.
[2] "Steam Boiler Economy," by Wm. Kent, p. 351.
[3] *U. S. Geol. Survey Bull.* **323**, p. 18.
[4] *J. Am. Chem. Soc.*, **30**, 1485 (1908).

TABLE I.

Expt. No.	Loss in weight		Total loss in weight (Average). Per cent.	Moisture weighed.		Total moisture (Average). Per cent.	Unsat. hydrocarbons.	
	1st hr. Per cent.	2nd and 3rd hrs. Per cent.		1st hr. Per cent.	2nd and 3rd hrs. Per cent.		1st hr. Per cent.	2nd and 3rd hrs. Per cent.
				75°				
1	1.43	0.14	....	1.46	0.17	....	....	....
2	1.56	0.09	....	1.56	0.08	....	....	
3	1.45	0.12	....	1.46	0.20	....	....	....
Aver.	1.48	0.12	1.60	1.49	0.15	1.64	....	....
				100°.				
1	1.66	G 0.02	....	1.84	0.14	....	....	....
2	1.55	G 0.05	....	1.74	....	....	....	....
3	1.67	G 0.05	....	1.89	0.07	....	....	....
Aver.	1.63	G 0.04	1.59	1.82	0.10	1.92	....	....
				110°.				
1	1.65	G 0.09	....	1.89	0.12	....	....	....
2	1.73	G 0.05	....	1.84	0.04	....	....	....
3	1.65	G 0.09	....	1.85	0.13	....	....	....
Aver.	1.68	G 0.08	1.60	1.86	0.10	1.96	....	....
				120°.				
1	1.75	G 0.16	....	2.01	0.22	....	0.09	0.22
2	1.72	G 0.16	....	1.98	0.19	....	0.09	0.07
3	1.70	G 0.06	....	1.87	0.19	....	0.04	0.22
Aver.	1.72	G 0.13	1.59	1.95	0.20	2.15	0.07	0.17

taken place to some extent. Our method failed to detect any unsaturated hydrocarbons.

At 110° the moisture weighed was 0.18% greater than the loss in weight of the coal. The gain in weight of the coal during the second and third hours is greater than at 100° showing more oxidation. Another point worth noting is that an appreciable amount of the moisture remains in the coal after the first hour's heating at this temperature.

The results at 120° show the moisture weighed to be 0.23% greater than the loss in weight of the coal during the first hour. The oxidation during the second and third hours is appreciably more than for 100° at this temperature, and we have an appreciable amount of hydrocarbons evolved, but this is much more marked during the second and third hours.

The amount of moisture given off during the second and third hours is considerable, being about 10% of the total moisture. If we wish to obtain some idea of the oxidation we must add to the difference between the moisture weighed and the loss in weight of the coal (0.56%) the weight of unsaturated hydrocarbons found (0.17%) giving 0.73% of the weight of the coal, a value which must be low, as we know other gases, as well as hydrocarbons, are given off.

The results obtained by heating the coal for the fourth and fifth hours, and again for the sixth, may be briefly summarized. The coal tube continues to gain in weight, but the gain is much less than for the second and third hours. A small amount of hydrocarbons appears to be given off at 110°. The moisture weighed is almost negligible even at 75°. All that can be driven off at this temperature disappears during the first three hours.

It would appear therefore from these experiments with the soft coal that in the determination of moisture as usually carried out, a considerable amount of moisture is left in the coal—at least 10% of the total moisture. If however the temperature is raised until this moisture is expelled, an appreciable amount of hydrocarbons in addition to other gases will be driven off. Oxidation of some constituents of the coal takes place causing an increase in weight, which may be estimated at about 0.80% of the weight of the coal.

We pass now to the results obtained by heating the coal in a current of dry nitrogen. The nitrogen was prepared by passing air through ammonia water and then over heated copper. The results are tabulated as in the previous experiments.

TABLE II.

Expt. No.	Loss in weight		Total loss in weight (Average). Per cent.	Moisture weighed.		Total moisture weighed (Average). Per cent.	Unsatd. hydrocarbons.	
	1st hr. Per cent.	2nd and 3rd hrs. Per cent.		1st hr. Per cent.	2nd and 3rd hrs Per cent.		1st hr. Per cent.	2nd and 3rd hrs. Per cent.
				75°.				
1	1.63	0.13	....	1.40	0.06	....	....	....
2	1.58	0.08	....	1.44	0.20	....	....	....
3	1.61	0.10	....	1.42	0.18	....	....	....
Aver.	1.61	0.10	1.71	1.42	0.15	1.57	....	....
				100°.				
1	1.93	0.01	....	1.74	0.18	....	....	....
2	1.89	0.08	....	1.76	0.06	....	....	....
3	1.87	0.03	....	1.74	0.14	....	....	....
Aver.	1.90	0.04	1.94	1.75	0.13	1.88	....	....
				110°.				
1	1.99	G 0.05	....	1.84	0.04	....	....	....
2	1.87	G 0.03	....	1.82	0.14	....	....	....
3	1.92	....	....	1.84	0.09	....	....	....
Aver.	1.93	G 0.03	1.90	1.83	0.09	1.92	....	....
				120°.				
1	1.94	G 0.01	....	1.90	0.23	....	0.10	0.36
2	1.93	G 0.03	....	1.90	0.03	....	0.10	0.22
3	1.89	G 0.01	....	1.84	0.09	....	0.00	0.03
Aver.	1.92	G 0.02	1.90	1.88	0.12	2.00	0.07	0.20

At 75° the loss in weight of the coal was 0.14% greater than the moisture weighed. A separate test made showed that 0.08% of carbon dioxide was evolved from this coal when heated.

The results for 100° show that the loss in weight of the coal during the first hour's heating was greater by 0.15% than the moisture weighed. During the second and third hours' heating, however, the moisture weighed is greater then the loss in weight of the coal. This suggests the synthesis of some water from the hydrogen and oxygen in the coal. An appreciable amount of moisture is left in the coal after the first hour's heating.

The results for 110° show the same variations as those for 100°. The moisture weighed is still less than the loss in weight of the coal, but the difference is now very small. At 120° the total moisture weighed for three hours is slightly greater than the loss in weight of the coal. Doubtless an appreciable amount of gas must have been driven off; in fact the amount of heavy hydrocarbons is large enough to be detected. Oxidation must have taken

place to a considerable extent. Water is still retained after an hour of heating.

If we assume that the difference between the loss in weight of the coal when heated in nitrogen, and when heated in air, represents the oxidation, we can express the oxidation for the first hour in percentage values of the moisture, as follows:

TABLE III.

	Per cent.
At 75°.....	8.72
At 100°.....	14.84
At 110°.....	13.44
At 120°.....	10.26

The moisture in the bituminous coal was also determined at the different temperatures in the official way, *viz.*, by heating one-gram samples in platinum crucibles for one hour. The results follow:

TABLE IV.

	Moisture, official method.		
Temp.	No. I. Per cent.	No. II. Per cent.	Total "moisture weighed" from Table I. Per cent.
75°	1.12	1.07	1.64
100°	0.95	1.01	1.92
110°	1.32	1.39	1.96
120°	1.25	1.29	2.15

The true moisture in the coal is therefore greater than the moisture found by the official method by 50% of the total moisture.

It appears from Tables I–IV that the moisture determination, as usually carried out, is in error from several causes: firstly, as shown in Table III, the value is too small by 14% of the moisture, due to an increase in weight of the coal, caused probably by oxidation, which is far from being balanced by the loss of occluded gases; and secondly, due to the water that still remains in the coal, which, considering Table IV, amounts to about 26% of the total moisture; the two errors combined amount to 40% of the true moisture.

We now come to the experiments with the anthracite coal. In the first place, we will consider the results obtained by heating the coal in dry air.

TABLE V.

No. of Expt.	Loss in weight. 1st hr. Per cent.	Loss in weight. 2nd and 3rd hrs. Per cent.	Total loss in weight (Average). Per cent.	Moisture weighed. 1st hr. Per cent.	Moisture weighed. 2nd and 3rd hrs. Per cent.	Total moisture (Average). Per cent.	Carbon dioxide. 1st hr. Per cent.	Carbon dioxide. 2nd and 3rd hrs. Per cent.
1	2.60	0.07	...	2.63	0.07	....	0.23	none
2	2.57	0.07	2.65	2.64	0.10	2.72	No determination.*	
1	2.60	0.03	....	2.62	0.22	....	0.16	none
2	2.67	0.03	2.67	2.70	0.19	2.86	0.14	0.07
1	2.64	0.04	....	2.64	0.31	....	0.15	0.07
2	2.63	0.03	2.67	2.63	0.13	2.86	0.18	none
1	2.73	G 0.11	....	2.62	0.11	....	0.16	0.11
2	2.73	G 0.06	2.65	2.66	0.05	2.72	0.26	none

* Tare was broken during the run.

The carbon dioxide was determined for all the following experiments by absorbing the gas in potassium hydroxide solution. The further determination of the hydrocarbons was not attempted. As heretofore the results are percentage values of the original weight of coal.

It is noted that in the case of both coals the moisture weighed is greater than the loss in weight of the coal. The water is much more easily expelled from the anthracite coal, as it is almost entirely driven off during the first hour of heating, while with the soft coal this was not the case.

The next series of results was obtained by heating the anthracite coal in an atmosphere of nitrogen.

TABLE VI.

Expt. No.	Loss in weight. 1st hr. Per cent.	Loss in weight. 2nd and 3rd hrs. Per cent.	Total loss in weight (Average). Per cent.	Moisture weighed. 1st hr. Per cent.	Moisture weighed. 2nd and 3rd hrs. Per cent.	Total moisture (Average). Per cent.
			75° C.			
1	2.77	0.02	...	2.48	0.05	....
2	2.77	0.01	...	2.41	0.06	....
3	2.74	0.01	2.77	2.45	0.00	2.47
			100° C.			
1	2.84	0.03	....	2.31	0.00	....
2	2.77	0.04	..	2.51	0.00	.
3	2.79	0.10	2.83	2.35	0.00	2.39
			110° C.			
1	2.81		....	2.64	....	....
2	2.76		....	2.61	.	....
3	2.86		2.81	2.64	....	2.62
			120° C.			
1	2.85	..	....	2.54	....	....
2	2.83	..	....	2.45	....	....
3	2.83	.	2.84	2.53	....	2.51

The moisture weighed is appreciably less than the loss in weight of the coal. The difference is about 0.31%, while the carbon dioxide given off according to the previous experiments was 0.23%. The difference between these values, or 0.08%, represents roughly the unidentified gases.

As was the case when the coal was heated in air, practically all the moisture is driven off during the first hour of heating. The amount of this moisture is almost the same for 75° as for 120°.

The analysis of the anthracite according to the official method gave the following results:

TABLE VII.

	Moisture by official method.		
Temp.	No. I. Per cent.	No. II. Per cent.	Total "moisture weighed" from Table V. Per cent.
75°	2.37	2.40	2.72
100°	2.30	2.37	2.87
110°	2.39	2.42	2.88
120°	2.40	2.40	2.72

The moisture as found by the official method is here only from 15% to 20% less than the moisture weighed.

The bituminous coal and the anthracite were both

analyzed for iron, sulfur, volatile matter and ash. The results follow:

TABLE VIII

Constituent	Bituminous coal. Exp. I. Per cent	Bituminous coal. Exp. II Per cent	Anthracite Exp. I. Per cent.	Anthracite Exp. II Per cent
Iron	0.65	0.55	0.48	0.58
Sulfur	1.02	1.07	1.15	1.18
Vol. matter.....	32.49	31.80	5.77	6.13
Ash.....	6.83	6.74	8.37	8.34

We see from these experiments that the greater oxidation in the case of soft coal could scarcely be due to the greater amounts of iron and sulfur present, as these constituents are present to almost an equal amount in the two cases. Rather, the greater oxidation must be due to the fact that the moisture is not so rapidly expelled from the soft coal.

The curves shown in Figs. A and B serve to indicate very clearly the general character of the results. The temperatures are plotted as abscissae and the per cent. of moisture as ordinates. The curves of Fig. A represent the results for the bituminous coal, those of Fig. B the results for the anthracite. The total decrease in weight of the coal during the first three hours, which is shown in curve I of Fig. A is practically the same for all the different temperatures, the curve being practically a straight line. Curve II shows the gradual increase in moisture given off by the coal as the temperature rises. Here too we have practically a straight line. Curve III represents the variation in the weight of the bituminous coal when heated for three hours at the different temperatures, in nitrogen. For temperatures above 100° the weight is constant. This curve lies throughout its whole length far above Curve I, showing the effect of oxidation when the coal is heated in air. The relation of the amount of moisture given off to the temperature when the coal is heated in nitrogen is set forth by Curve IV. The upper portion of the curve lies a little below Curve II. This could be accounted for by assuming the synthesis of a small amount of water from the oxygen of the air and hydrogen present in the coal.

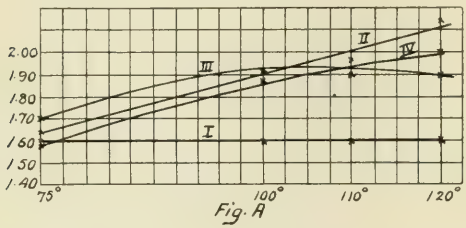

Fig. A

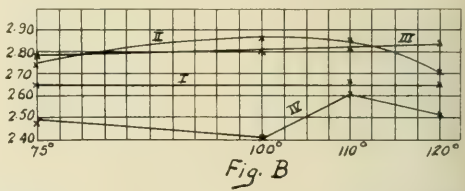

Fig. B

The curves for the anthracite (Fig. B) resemble in some respects those for the bituminous coal. Curve I, showing the relationship between the change in weight of the coal and the temperature at which it is heated (in a current of air), is a straight line, as in the case of the soft coal. The total moisture given off by the coal when heated in air shows a maximum at about 105° (Curve II). From Curve III we see that there is a continual loss in weight of the coal when heated in nitrogen, but this is not much greater for 120° than for 75°. Curve IV showing the moisture weighed at the different temperatures is more difficult to draw than the others as the results are not as regular. Obviously the result for 100° is worthless. However, for the sake of completeness the points are indicated.

The above considerations show that the errors made in the determination of moisture by the official method are much more serious in the case of bituminous coal than for anthracite. The determination being of little value in the former case, as at present carried out, we suggest that for this class of coals the method be modified, and that the coals be heated in a current of dry air at a temperature of at least 110°, the moisture given off being weighed directly after absorbing it by anhydrous granular calcium chloride. The results for one coal would then be comparable with those of another while at present this is not the case.

SUMMARY.

We may briefly summarize our results as follows:

(1) When the determination of moisture in coals is carried out according to the official method, the result is much lower than it should be, the error amounting in the case of some bituminous coals to 40% of the true moisture.

(2) The oxidation of iron or sulfur or both, and the non-expulsion of a considerable part of the water which probably accounts for the largest errors here involved, are much greater in the case of bituminous coal than with anthracite: due on the one hand to the moisture remaining in contact with the coal at a high temperature for a much longer time, and further to the more porous nature of the softer coal.

(3) It was suggested that for bituminous coals the method be modified and that the coal be heated in a current of dry air at a temperature of at least 110°, the moisture given off being weighed directly, after absorbing it in anhydrous calcium chloride.

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A METHOD FOR THE UTILIZATION OF LEAD FURNACE FUME.

By L. S. HUGHES.

Received Dec. 18, 1911.

A large item of expense in the operation of lead smelting plants is the treatment of furnace fume. Where the so-called "open-hearth" furnaces are employed this by-product frequently amounts to more than twenty per cent. of the total ore charge and

arries approximately that proportion of the original metallic values.

Ordinarily, "open-hearth" furnaces are arranged in a single battery below a common flue which receives the fume from all the furnaces. This flue delivers into a series of collecting chambers in which the furnace dusts and ashes are deposited. The fan which supplies the necessary draft is placed beyond these chambers and the fume proper is forced by its exhaust into a cloth filter system of the bag room type which retains the solid fume and filters it from the furnace gases. From the filter bags the fume falls into a closed brick chamber and is allowed to accumulate there until it is several feet in depth. The pile is then set on fire and slowly smolders until the sulfide and carbonaceous ingredients are oxidized. This burning occupies several days and in order to avoid interruption of the furnace operation several independent filter systems are used so that any one may be cut off whenever it is necessary to burn the fume therein. When it is finished the fume is converted into a whitish cinder of approximately the following composition.

	Per cent.
Lead sulfate	55
Lead monoxide	44
Zinc oxide	1
Ferric oxide	traces

If a sufficient settling system has been employed between the furnaces and the bag room there will be no more than traces of the non-volatile constituents of the furnace charge.

Hitherto no better means of disposing of the burned fume has been devised than that of using it as a smelting material: most commonly by reduction in the blast furnace, but occasionally in an open-hearth furnace. Attempts have been made to use the unburned fume as a pigment and there is a small market for it in the paint trade, but its variable color and certain difficulties in its manipulation sharply limit the demand and the total tonnage thus consumed is too small to affect the problem.

The remarkable freedom of the fume from non-volatile impurities and the fact that it represents a mixture of almost absolutely pure oxidized lead compounds after burning, presented it as a promising raw material for conversion into lead compounds, but the problem proved by no means easy of solution.

An examination of the literature disclosed several processes devised for the conversion of lead sulfate to other compounds in the wet way. Some of these were manifestly worthless from a commercial standpoint as the inventors had proceeded with a reckless disregard of the cost of reagents: others, which appeared to be conceived in a spirit of practicality, were carefully checked experimentally.

While it was desired to find a plan which would yield a product of lead oxide or hydrate, compounds not only merchantable *per se*, but readily convertible by ordinary processes into an indefinite number of compounds, methods for the direct conversion of the sulfate or sulfate-containing mixture into compounds of special desirability, such as the chromates, were included in the list of possibly available methods.

Prior methods proved disappointing in every instance, and in some cases a most grievous discrepancy developed between the facts, as revealed by experiment, and the statements published. Even where the methods had been the basis for patents, instances were found which strongly indicated that the claimants had neglected empirical verification of their ideas.

Attempts were made to convert the pulverized cinder directly into lead chromate by treatment with a soluble chromate, but the products proved of unsatisfactory composition through the persistence of a portion of the lead sulfate and in all cases were of unsatisfactory color and tinctorial strength.

Digestion with sodium hydrate and carbonate as a preliminary step gave but slightly better results as it proved practically impossible to convert all the lead sulfate present.

As the amount of residual sulfate appeared larger when a coarsely pulverized cinder was employed, a microscopic examination of the digested fume was made, and this showed plainly that the residual sulfate was encysted by crusts of hydrate, the complex particles having much the structure of a nut with a kernel of unchanged sulfate and a shell of hydrate. This observation naturally suggested trituration as a means of effecting complete conversion and the employment of a closed ball mill entirely obviated this difficulty, conversion being rapidly and completely accomplished.

Up to this point little attention had been paid to the amount of reagents employed but for commercial application it was manifestly necessary that the treatment be systematized and the chemicals reduced to the minimum amount. "Soda lye" had been selected as the most generally desirable reagent for decomposition of the lead sulfate, both because of its low cost and because by adding it in dry form its heat of solution within the mill obviated any necessity for the employment of extraneous heat to accelerate reaction. In order to obtain a sufficiently high temperature and also to yield a sodium hydrate solution of sufficient concentration the water was proportionately reduced. A mechanical difficulty appeared in the first test: the solution of sodium sulfate resultant from the decomposition was supersaturated and the crystals of sodium sulfate interlaced the paste of lead hydrate converting the entire mass into a tough, coherent cake which had to be broken out of the mill by hand. From a practical standpoint it was impossible to remove it by solution of the sodium sulfate by treatment with water, for the cake was almost impermeable by water. It was noted that this solidifying action did not take place so long as the mill was in motion, but immediately after it came to rest the setting occurred. Repeated efforts were made to introduce water immediately after grinding had stopped, but in every instance the "setting" had taken place.

The solution of this difficulty was effected by intro-

ducing a new pattern in double cone ball-mills which permitted of the introduction of water and washing out of the charge without stopping the mill. The body of the mill was of the familiar type employed in horizontal mills, but the outlet was made considerably wider than the charging hole so that when the level of water within the mill was raised it would overflow at the outlet only. This proved of the greatest convenience and value in operating. After conversion was completed a jet of water was turned into the charging hole and the rotation of the mill continued. The hydrate in the form of an impalpable sludge was, of course, kept continually stirred up and was rapidly floated through the outlet into a washing vat. This water-floating action had the additional advantage that by no possibility could any portion of the charge escape from the mill before it was reduced to extreme fineness.

Washing was effected by decantation and the hydrate was then ready for conversion into other compounds.

For conversion into chromate it was dropped from the washing vat into a large percipitating vat and treated with the theoretical amount of acetic or nitric acid required for its conversion into a basic salt; water was added and the necessary solution of an alkaline chromate or bichromate. The extreme reactivity of the hydrate enabled the conversion to be effected without heating and with no more than the theoretical amount of acid.

For the production of oxides the hydrate was pumped into a filter press and the cakes furnaced without previous drying.

It was found possible to produce a good lead arsenate at a considerably lower cost than obtains with present processes by mixing the freshly made hydrate with a solution of arsenic acid obtained by oxidation of arsenious anhydride with nitric acid, and boiling. The reaction was a little slow but the product most satisfactory.

Other instances of easily obtainable compounds might be cited but the possibilities of lead hydrate are manifest.

While the method offers absolutely nothing new from a chemical standpoint, it promises to have a very considerable influence upon the lead pigment business on account of the great economy over present methods which it entails. The degree of saving effected by using a by-product such as "blue fume" and thus saving both the smelting cost of producing pig lead and the additional cost of furnacing the pig lead to litharge and pulverizing the litharge is apparent from the following tables:

The cost of producing chrome by present methods varies somewhat according to the market rates for litharge, acetic acid, nitric acid and sodium bichromate; the following figures represent usual costs in manufacturing on a large scale:

Cost per cwt.	
69 pounds litharge at 5½ c	$3.79
43½ pounds 56% acetic acid at 3½ c	1.38
46 pounds sodium bichromate at 5½ c	2.53
Labor	0.25
Water and fuel	0.05
Packages and packing	0.25
	$8.25

To this must be added freight and selling expense.

These figures are based on good practice without waste. Most manufacturers compute their cost of production at from $8.50–$8.75. For small producers who have to buy in small lots and at higher prices the cost is much higher.

COST OF PRODUCING CHROME UNDER NEW PROCESS.

Using the same basis of prices as before, the cost per cwt. is:

11 pounds caustic soda at 2 c	$0.22
80 pounds burned fume at 2½ c	2.00
29 pounds 56% acetic acid at 3½ c	1.38
46 pounds sodium bichromate at 5½ c	2.53
Labor	0.25
Water and fuel	0.05
Packages and packing	0.25
	$6.68

To this must be added freight and selling expense.

It will be observed that less acid is used than in the former statement. This is because of the much greater reactivity of lead hydrate as compared with litharge. The burned fume is valueless except as a smelting material: its value is therefore the value of the metal which can be recovered from it, less the smelting cost and freight.

A METHOD FOR TESTING OUT PROBLEMS IN ACID PHOSPHATE MANUFACTURE.[1]

By F. B. Porter.

Received Jan. 12, 1912.

The process of manufacturing acid phosphate is, like many other factory processes, very hard to carry out on a laboratory scale. The writer has at various times made attempts to do this on 1000 or more grams of rock dust.

It has so far been practically impossible to stir sufficiently and control the temperature well enough with the limited apparatus available to get satisfactory results.

This being the case we recently devised the plan of using the quantities of acid and rock required to make 2 grams of finished acid phosphate, stirring them together with a stirring rod in a test tube and using the entire product for the insoluble test.

The following is the method in detail: Weigh 1.100 grams of rock dust into a $5'' \times {}^{5}/_{8}''$ test tube, add the quantity of acid required from a small bore 1 cc. Mohr's pipette, allowing the pipette to run empty and draining for a definite length of time (1 minute).

The acid required and used is determined by titrating amounts delivered in the same way with half-normal alkali.

Stir the acid and rock together for 3 minutes, being careful to see that the dust is all wetted by the acid in the first half-minute of the stirring period. The test tubes thus prepared, without removing the stir-

[1] Presented at the forty-fifth meeting, American Chemical Society, Washington, December, 1911.

ng rod, are then held at any temperature for any me desired.

The resulting acid phosphate is transferred to a cm. filter paper with water and the citrate-insoluble iosphoric acid determined by the Official Method. age 3, *Bull.* **107,** Rev. Bureau of Chem.

At first this method gave occasional erratic results it with practice and care we are now able to get sults agreeing practically within the limit of error the citrate-insoluble method. The results used this kind of work are averages of three and in ost cases four separate analyses. In this way curate reliable results are obtained.

This method has many advantages over one using rger quantities of rock. Three of these are:

1st. Large numbers of tests can be carried out th inexpensive apparatus common to every laboratory.

2nd. The temperature at which the tests are held n be easily and accurately controlled.

3rd. A large number of these tests can be made the time required for one by any other method iown to the writer.

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ON THE DETERMINATION OF CARBON DIOXIDE IN SOILS.

By LEON T. BOWSER.

Received October 26, 1911.

Up to a comparatively recent time no method had en so thoroughly tried out as to be considered a liable one for small amounts of carbon dioxide in ils. In 1908, the Association of Official Agricultural iemists took up the matter of testing the applicality of the Knorr method, and in 1909 a still larger iount of coöperative work was done. The results the work will presently be presented in tabular rm.

The method outlined in the author's previous paper[1] ving been found to yield good results with materials ntaining a large percentage of carbon dioxide, it mained to be seen whether it would be as satisfactory cases where the percentage is small. As a preliminary, o determinations were made in a sort of artificial il containing a known amount of carbon dioxide. very pure sea sand was ignited for some time to move all organic matter and decompose such calcium rbonate as might be present from finely divided rticles of sea shells and other carbonate materials. iis was cooled, and to a weighed portion was added ough analyzed $CaCO_3$ to give exactly 0.05 per cent. O_2. A blank determination was first made on the ater, reagents, and freshly ignited sand; then two terminations were carried out on the artificial soil. ie blank first found was deducted from the titration sults, and CO_2 calculated from the difference. The terminations gave 0.043 and 0.048 per cent. CO_2, average of 0.0455 as against the 0.05 per cent. tually present, which seemed very satisfactory.

[1] THIS JOURNAL, **4,** 203–205 (March, 1912).

There was available a considerable quantity of each of the two samples for the 1909 A. O. A. C. soil work, and as the average of results from a large number of independent workers is likely to be somewhere near the truth, it was thought that here was an unusually good opportunity to compare the two methods. Four determinations were accordingly made on each of the two soils, under conditions parallel to those used by the A. O. A. C. workers, and the results are presented in Table I, accompanied by the Association results on the same.

TABLE I.

Soil 1.

	Knorr method Analyst.							Volumetric method.
	1.	2.	3.	4.	5.	6.	7.	
	0.070	0.085	0.072	0.092	0.092	0.080	0.074	0.080
	0.073	0.082	0.073		0.085	0.074	0.080	0.077
	0.065	.	0.075		0.085	0.080	...	0.075
	0.072		.		0.082	0.080	. .	0.084
	0.068	.			0.085	. .	...	...
	0.073	.		.	...	. .	...	...
Av.	0.070	0.083	0.073	0.092	0.086	0.079	0.077	0.079

General av. 0.078

Soil 2.

	Analyst.							
	1.	2.	3.	4.	5.	6.	7.	
	0.027	0.027	0.023	0.027	0.027	0.036	0.026	0.026
	0.028	0.035	0.021		0.027	0.036	0.025	0.031
	0.031	0.028	0.023		0.030	0.030	. .	0.031
	0.024	0.035	0.020		. .	. .	...	0.026
	0.027	...	0.022		. .	. .	...	...
Av.	0.027	0.031	0.022	0.027	0.028	0.034	0.025	0.028

General av. 0.028

Comparison of Averages.

	Soil 1.	Soil 2.
A. O. A. C.....	0.078	0.028
Volumetric.....	0.079	0.028

The averages given in the Association report are: No. 1, 0.081 per cent.; No. 2, 0.027 per cent. CO_2, but these include only the results of the first five analysts, the latter two reporting too late to be included. For the present work all of the results are considered, increasing the probability that the averages are near the truth. The agreement between these revised averages and the ones obtained by the volumetric method is remarkably close, and shows that the latter is thoroughly reliable. On the score of consistent results, the volumetric method is superior to the gravimetric. Thus on Soil 1 the A. O. A. C. results range from 0.065 to 0.092, a variation of 0.027 per cent., while the volumetric results range from 0.075 to 0.084, a variation of 0.009 per cent., or just one-third of the former. On Soil 2, the A. O. A. C. results run from 0.020 to 0.036, a variation of 0.016 per cent., as against 0.026 to 0.031, a variation of 0.005 per cent. for the volumetric, which, as with Soil 1, is practically one-third as great a difference.

The method followed was as outlined in the preceding paper,[1] and in each case 10 grams of soil were taken. Soils containing 0.1 per cent. or less of CO_2 require for titration an acid of strength not exceeding $N/50$, since when stronger acids are used the evolved CO_2 is equivalent to but a fraction of one cc., and too

[1] THIS JOURNAL, **4,** 203.

great an error is thus introduced. Occasion may even arise where a centinormal acid is demanded, although the writer has never encountered such a case. Even with $N/50$ acid a considerable amount of care is necessary in observing end points, and the use of comparison solutions is advisable.

There are many ways in which this method seems especially adapted to soil work. Thus boiling the sample in the flask does not cause even the slightest bumping, and the evolved gas comes off smoothly and uniformly. Also, the vigorous boiling possible in this form of apparatus insures a thorough and constant stirring up of the sample, with consequent complete decomposition of the carbonates. One precaution which must be carefully observed, however, is in regard to the degree of heat applied to the flask at first. Just as the contents are about to begin ebullition there is a tendency to froth, and the flame should be turned down low for a moment until the solution is in full boiling.

A curious fact has been noted by several analysts in connection with the amount of a soil sample which should be introduced into the decomposing flask; results with 10 grams of soil are almost invariably higher than those with larger amounts. This is illustrated in Table II, where three independent analysts have obtained results decidedly similar.

TABLE II.

	Soil 1.			Soil 2.			
	50 gms.	35 gms.	10 gms.	50 gms.	40 gms.	20 gms.	10 gms.
Analyst 6	0.065	..	...	0.021	..	..	...
Analyst 7	...	...	...	...	0.025	0.0225	...
A. O. A. C. Av.	...	...	0.078	...	...	...	0.028
L. T. Bowser	...	0.061	0.079	0.025	..	...	0.028

An investigation into the causes of this behavior might yield results of considerable value.

Judging from the results secured, the titration method is apparently superior to the procedures now in use for the determination of carbon dioxide in soils. It is far more accurate, the manipulation simpler, results more uniform, and the apparatus itself not in the least fragile. These advantages, coupled with the fact that there are very few precautions to be observed, should make it of great service in the analysis of soils.

In conclusion, the writer desires to acknowledge his indebtedness for many favors to Mr. J. W. Ames, of the Ohio Agricultural Experiment Station, Mr. W. F. Pate, formerly of the same place, and Dr. A. M. Peter, of the Kentucky Station.

THE PHENOMENON OF THE APPARENT DISAPPEARANCE OF THE HIGHER BOILING PHENOLS IN CREOSOTED WOOD AND ITS EXPLANATION.

By SAMUEL CABOT.

Received January 18, 1912.

One of the mysteries of the chemistry of wood preservation is the apparent disappearance of the phenols from timber impregnated with coal tar creosote. The generally accepted explanation has been that carbolic acid and the cresols are volatile and soluble. Most authorities have been content with this explanation. From the logic of the fact, however, it does not seem to cover the more complex members of the series. Some of those found in creosote are non-volatile without decomposition under ordinary pressure and have been carried over into the distillate by the oil. These phenols are also less soluble than the bases which are found in old treated timber. In an earlier article it has been shown that the phenols are, if anything, less subject to evaporation than the oil fraction in which they are contained.

The only solution to their apparent disappearance would seem to be that they have been so altered in the process of time that they no longer can be found by the regular method of analysis. In accordance with this theory, experiments were conducted with a view of following and detecting the changes in the phenols of a high-boiling oil on exposure to the air.

First, the freshly distilled oil containing 7.2 per cent. of tar acid was exposed. It changed with considerable rapidity from a clear reddish color to a brownish black. The same oil with the phenols removed changed very slightly.

On extracting the tar acids from the blackened oil in the ordinary way with dilute caustic soda, it became much lighter in color and a black tarry layer separated out between the oily and aqueous liquids. This tarry substance was insoluble in benzole and only very slightly soluble in water, though readily so in acetone.

On weighing the phenols and tarry matter the results showed phenols, 6.77 per cent.; tarry matter, 0.47 per cent. The original freshly distilled clear oil when shaken with caustic soda precipitated no tarry material.

In the next tests some high-boiling tar acids were exposed on a watch glass for six months. The original phenols were entirely soluble in benzole. Those that had been exposed to the air, however, were only partially so, though readily soluble in acetone. A portion of that soluble in benzole was re-exposed for a period of two months. Again it became partially insoluble. The rest was analyzed for phenols in the usual way. It precipitated a tarry layer with caustic soda equal to 53% of its weight; the remaining 47 per cent. were recovered from the acidified liquid. The tarry products from both these experiments had a sharp acid taste much stronger than that of the oil. This tarry substance is curious in its behavior. A portion of it, while insoluble in caustic soda solution is soluble in water, resembling in this respect a soap. After the water-soluble portion has been washed out, some of the remainder becomes soluble again in the original oil or benzole. This can be partially, though not completely reprecipitated by the alkali. The remainder which is insoluble in either water or benzole is not changed in this respect by neutralizing with acid.

It would appear from these facts that the phenols

through three stages of oxidation: (1) To a prodet insoluble in a 10 per cent. alkali solution, but luble as an alkali salt in water. (2) Being further idized to a product which will form a salt with alkali, but hydrolyzes on dilution; in other words, able only in an excess of caustic soda. (3) The d product with a very slight affinity for caustic da, probably held in solution in the oil only by the nchanged and partially changed phenols. The origil tarry matter on being heated cokes very easily, sing only about 15 per cent. of its weight.

The methods used to extract the oil from impregted timber for analysis have been, so far as I have en able to find out, to treat (1) with benzole, (2) with luole, (3) with ether, and (4) with absolute alcohol.

It will be noted that the first three methods could t extract the final oxidation product of the phenols, nereas the last one could. Nevertheless, the exact from the last method would show only a trace phenols by the ordinary test because the common actice of distilling the oil before analysis would ke or decompose the oxidized phenols.

An extraction was made of some chips from the rface of a creosoted tie which had been in the ground om 1879 to 1906 and exposed to the air from then til 1911. Twenty grams of this wood completely tracted with benzole gave 0.78 gram of oil. This as redissolved in benzole and extracted with caustic da. It gave a trace of phenols and 0.014 gram of rry matter, or about 1.8 per cent. on the oil. The ood was then extracted with acetone. It gave 63 gram of a black, pitchy mass, a small portion which was soluble in ether, but the whole readily luble in absolute alcohol. It was slightly soluble caustic soda, giving a yellowish coloration and a stinct, pyridine smell. It was sharp to the taste, sembling coal tar. On heating, it gave off a small mount of pungent gas, the remainder turning to coke. This acetone extract probably contained some henolic and basic products and some oxidized hydrorbons, and a slight amount of resin dissolved from e wood.

The above experiments seem to show that the higher al tar phenols will not volatilize from creosoted ood, but remain as more complex oxidation prodts insoluble and non-volatile in character and esumably with good antiseptic qualities, though nether these have been impaired or improved by e change is yet to be determined. At any rate, ese oxidized phenols would seem to have to a conlerable degree the three properties of prime imrtance in a wood preservative, namely, non-volaity, antiseptic qualities and insolubility.

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THE FLUIDITY OF FISH OIL MIXTURES AS AN ADDITIVE PROPERTY.

By GEORGE F. WHITE.

Received December 4, 1911.

The increasing adulteration of vegetable oils by h oils as well as the substitution of one fish oil by another, has called forth many attempts to detect such practices in recent years. In many instances the chemical properties of the two oils so closely approximate each other that the ordinary commercial methods of analysis fail to distinguish either in a mixture of the two. Thus, it is known that dogfish liver oil may be offered as a substitute for cod liver oil without danger of discovery, especially when the oils are refined. Ordinary cod oil, used to a large extent for such purposes as currying, frequently consists of nothing but dogfish, shark, hake, or polluck oil. Menhaden oil is often used to replace whale and cod oils.

In order to definitely establish the fact that a certain sample of oil is a mixture, a great number of tests must be made, and, of course, these are of value only as they are accurate enough to detect small amounts of one oil in the other. A great quantity of data has been published on the viscosity of oils, from which many conflicting and erroneous conclusions have been drawn with respect to the connection

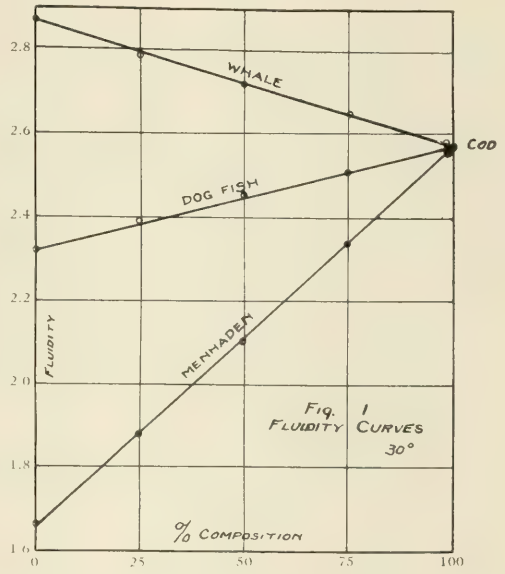


Fig. 1
FLUIDITY CURVES
30°

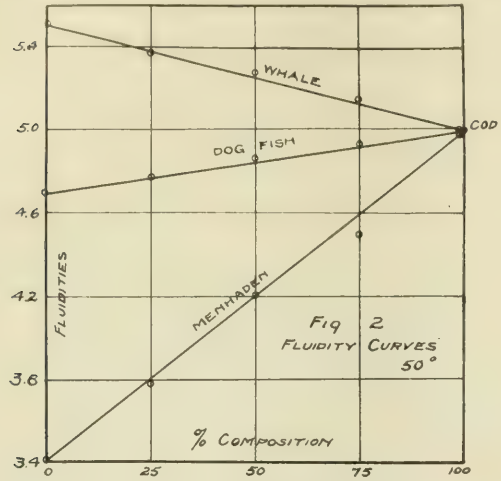
between this physical property and the composition of the oil investigated. Thus Kessler and Mathiason,[1] in a paper "On the Interpolation Method of Oil Analysis," in discussing the properties of oil mixtures, state that "neither the viscosity nor the fluidity of such solutions are necessarily additive, even though there is no evidence to indicate that either chemical or molecular compounds are formed." This statement is directly contrary to the views of Bingham[2] who believes that the fluidity of a mixture of two liquids, which do not react chemically with each other, is the sum of the partial fluidities of the components.

The object of this investigation was to test the above theory by mixing various fish oils with each other in definite proportions by weight and studying

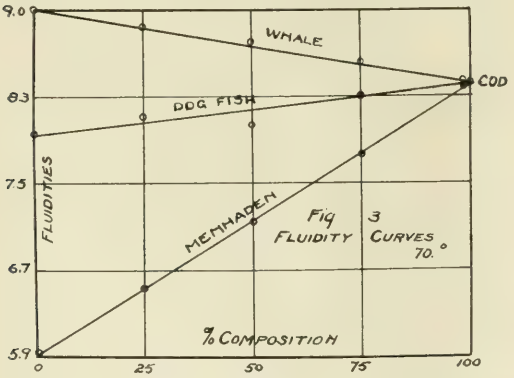
[1] THIS JOURNAL, 3, 66 (1911).
[2] Z. physik. Chem., 66, 1 (1909).

any relations between composition and viscosity or fluidity which might become evident.

The correct relationship between viscosity and composition can be established only by use of a viscosimeter which shall be accurate to at least one



per cent. The various instruments in use have been criticized in previous articles[1] and it is not necessary at this time to review their faults. The viscosimeters devised by Thorpe and Rodger,[2] by Bingham and White,[3] and the modification of these latter described by the author of this article[4] all seem well suited to the problem mentioned, as they all give results which probably may be relied upon as having less than 0.2 per cent. error. The viscosimeter used in a study of the viscosity of fish oils recently described[5] was used to measure the viscosity of the fish oil mixtures, since the time required for a determination (from



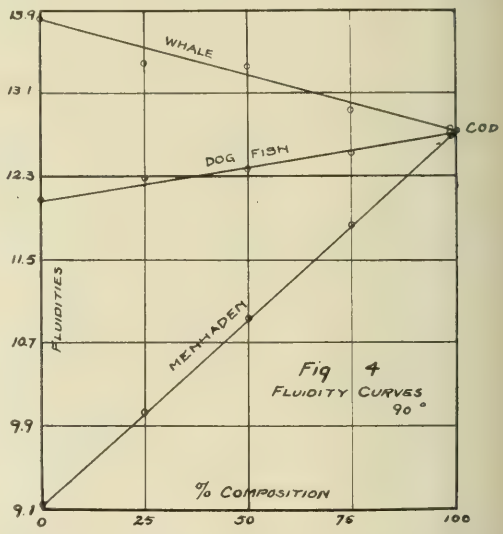
two to six minutes) was the most favorable for accurate work.

The whale and white cod liver oils, which were taken for use in this investigation, were commercial samples, while the menhaden and dogfish (Mustelus canis) liver oils were extracted from fish obtained at Woods Hole, according to the previously described method. The mixtures were made up by weight and allowed to stand at least twenty-four hours before analysis, to secure complete homogeneity. Following is a table giving a few of the common constants obtained, the saponification and acid numbers being expressed as the number of milligrams of potassium hydroxide required for one gram of oil.

TABLE I.

Oil.	Cod liver.	Whale.	Menhaden.	Dogfish liver.
Iodine No. (Hübl).....	142.60	156.60	128.10	135.90
Saponification No.....	185.80	192.80	16.26	193.00
Acid No.....	1.82	6.60	6.83	0.94

In the tables below are given the results of viscosity determinations expressed in absolute units, together with the fluidity calculated from the average viscosity.



Specific-gravity determinations of the pure oils were made in a pycnometer, no measurements being taken on the mixtures as the densities of these are nearly enough additive to allow proper calculation of the small kinetic energy correction $\frac{vd}{8\pi tl}$ in the following formula, used to obtain the viscosity values

$$\eta = \frac{\pi r^4 pt}{8vl} - \frac{vd}{8\pi tl}.$$

η is the viscosity, l the length and r the radius of the capillary tube, d the density of the oil, and v the volume of oil passing through the tube; p is the pressure to which the oil is subjected, and t is the time of flow.

TABLE II.—COD LIVER OIL.

Temp.	Viscosity.				
Degrees.	Rt. limb.	L. limb.	Av.	Fluidity.	Sp. gr.
30	0.3886	0.3882	0.3884	2.575	0.9277
50	0.2001	0.2005	0.2003	4.992	0.9149
70	0.1187	0.1189	0.1188	8.396	0.9008
90	0.07862	0.07882	0.07872	12.710	0.8900

[1] *Biochem. Z.*, **37**, 482 (1911); THIS JOURNAL, **4**, 106 (1912).
[2] *Phil. Trans.*, **185A**, 307 (1894).
[3] *J. Am. Chem. Soc.*, **33**, 1257 (1911).
[4] See Note 2.
[5] THIS JOURNAL, **4**, 106–107 (1912).

TABLE III.—DOGFISH LIVER OIL.

Temp. Degrees.	Viscosity. Rt. limb.	L. limb.	Av.	Fluidity.	Sp. gr
30	0.4319	0.4319	0.4319	2.315	0.9185
50	0.2133	0.2138	0.2136	4.682	0.9057
70	0.1262	0.1259	0.1261	7.931	0.8932
90	0.08272	0.08293	0.08283	12.080	0.8796

TABLE IV.—MENHADEN OIL.

30	0.6012	0.6025	0.6019	1.661	0.9371
50	0.2936	0.2938	0.2935	3.407	0.9234
70	0.1683	0.1683	0.1683	5.945	0.9097
90	0.1097	0.1096	0.1097	9.107	0.8965

TABLE V.—WHALE OIL.

30	0.3493	0.3477	0.3485	2.869	0.9192
50	0.1819	0.1824	0.1822	5.489	0.9063
70	0.1103	0.1099	0.1101	9.090	0.8912
90	0.07243	0.07238	0.07241	13.810	0.8782

TABLE VI.—MENHADEN-COD LIVER OIL MIXTURES.

Temp. Degrees.	Viscosity. Rt. limb.	L. limb.	Av.	Fluidity.
	1 Per cent. Menhaden.			
30	0.3904	0.3900	0.3902	2.563
50	0.2006	0.2008	0.2007	4.983
70	0.1199	0.1198	0.1199	8.340
90	0.07878	0.07895	0.07887	12.680
	25 Per cent. Menhaden.			
30	0.4284	0.4300	0.4292	2.330
50	0.2223	0.2223	0.2223	4.482
70	0.1295	0.1297	0.1296	7.716
90	0.08429	0.08429	0.08429	11.860
	50 Per cent. Menhaden.			
30	0.4765	0.4760	0.4763	2.099
50	0.2394	0.2398	0.2392	4.181
70	0.1405	0.1405	0.1405	7.117
90	0.09118	0.09126	0.09122	10.960
	75 Per cent. Menhaden.			
30	0.5331	0.5358	0.5344	1.871
50	0.2657	0.2646	0.2652	3.771
70	0.1535	0.1532	0.1534	6.519
90	0.09959	0.09943	0.09951	10.050

TABLE VII.—DOGFISH LIVER-COD LIVER OIL MIXTURES.

Temp. Degrees.	Viscosity. Rt. limb.	L. limb.	Av.	Fluidity.
	1 Per cent. Dogfish.			
30	0.3893	0.3903	0.3898	2.569
50	0.2004	0.2005	0.2005	4.987
70	0.1188	0.1188	0.1188	8.417
90	0.07904	0.07879	0.07892	12.670
	25 Per cent. Dogfish.			
30	0.3995	0.3996	0.3996	2.502
50	0.2037	0.2033	0.2035	4.914
70	0.1209	0.1211	0.1210	8.264
90	0.08000	0.08022	0.08011	12.480
	50 Per cent. Dogfish.			
30	0.4075	0.4090	0.4082	2.450
50	0.2060	0.2059	0.2060	4.854
70	0.1249	0.1247	0.1248	8.013
90	0.08114	0.08132	0.08123	12.310
	75 Per cent. Dogfish.			
30	0.4187	0.4203	0.4195	2.384
50	0.2099	0.2101	0.2100	4.762
70	0.1227	0.1224	0.1226	8.157
90	0.08146	0.08156	0.08151	12.270

TABLE VIII.—WHALE-COD LIVER OIL MIXTURES.

Temp. Degrees.	Viscosity. Rt. limb.	L. limb.	Av.	Fluidity.
	1 Per cent. Whale.			
30	0.3883	0.3852	0.3868	2.585
50	0.1995	0.1994	0.1995	5.013
70	0.1189	0.1187	0.1188	8.417
90	0.07855	0.07845	0.07850	12.740

TABLE VIII *Continued*

Temp. Degrees.	Viscosity. Rt. limb.	L. limb.	Av.	Fluidity.
	25 Per cent. Whale.			
30	0.3777	0.3777	0.3777	2.648
50	0.1944	0.1946	0.1945	5.141
70	0.1156	0.1157	0.1157	8.643
90	0.07754	0.07754	0.07754	12.900
	50 Per cent. Whale.			
30	0.3686	0.3689	0.3688	2.711
50	0.1898	0.1894	0.1896	5.274
70	0.1134	0.1131	0.1133	8.827
90	0.07495	0.07491	0.07493	13.340
	75 Per cent. Whale.			
30	0.3598	0.3596	0.3597	2.780
50	0.1863	0.1865	0.1864	5.365
70	0.1120	0.1115	0.1118	8.945
90	0.07480	0.07468	0.07474	13.380

The results are shown graphically in Figs. 1–5. In Figs. 1–4, fluidities of the oils are plotted as ordinates against composition of the mixtures as abscissas, the abscissas reading in percentages of cod oil; the four plots are taken from the fluidity readings at 30°, 50°, 70°, and 90°, respectively.

The fluidity curves are seen to be linear, and consequently it must be concluded that the fluidities of these oil mixtures are strictly additive over the range of temperature studied. According to what has been said, this confirms in a striking manner Bingham's fluidity hypothesis, which requires the above relationship between fluidity and composition in non-associated liquids. It has been indicated in a previous article[1] that these oils are slightly associated, the fluidity-temperature curve not being a straight line; but the deviation from a linear function is very slight, and scarcely to be taken into consideration in this connection. Therefore, if the fluidity of a mixture of two oils is measured, and that of the constituents is known, the composition of the mixture may be calculated. It has been shown[2] that the viscosity of these oils is characteristic and fairly constant if the different samples of oil are obtained under similar conditions; fluidity data should then add to the knowledge desired, regarding the detection of adulteration in oils. Of course, taken alone, the fluidity would hardly be of great value in detecting any such adulteration, but when considered along with the results of other tests simultaneously applied, it furnishes additional evidence concerning the character of the oil studied.

The mixtures of one part of one oil to ninety-nine of the other were made up to test the accuracy and delicacy of the method. The introduction of this one per cent. of oil was readily detected by the viscosimeter used, and the fluidity of these mixtures was found to conform to the additive relationship.

Since the fluidities are found to be additive, the viscosity should be a hyperbolic function of the composition. The relation between the viscosity and the composition is shown graphically in Fig. 5, the temperature being 30°. The curve for the menhaden-cod mixtures deviates markedly from a straight line, that for the dogfish-cod mixtures less so, while the viscosity

[1] THIS JOURNAL, **4**, 109 (1912).

[2] *Ibid.*

of the whale-cod mixtures presents a linear function. The menhaden oil has a viscosity which varies from that of the cod to the greatest extent of any of the oils, and we should expect that curve to evidence the greatest curvature. These facts coincide with the following mathematical deduction of the relation between fluidity and composition suggested by Bingham.

Since the fluidity is a linear function of the composition, this may be expressed by the formula

$$\varphi = \varphi_1 + (\varphi_2 - \varphi_1)x \qquad (1)$$

where φ represents the fluidity of the mixture, φ_1 and φ_2 that of the two components, the latter being supposed to be the more fluid, and x the percentage of the latter in the mixture. The corresponding viscosity equation is

$$\frac{1}{\eta} = \varphi_1 + (\varphi_2 - \varphi_1)x,$$

where φ_1 and φ_2 are constants and η and x are variable, or

$$\eta = \frac{1}{\varphi_1 + (\varphi_2 - \varphi_1)x}. \qquad (2)$$

The curvature is therefore

$$K = \frac{2(\varphi_2 - \varphi_1)^2[\varphi_1 + (\varphi_2 - \varphi_1)x]^3}{\{[\varphi_1 + (\varphi_2 - \varphi_1)x]^4 + (\varphi_2 - \varphi_1)^2\}^{\frac{3}{2}}}. \qquad (3)$$

By differentiating this curvature in respect to the concentration x, and equating to zero, we obtain the concentration where the curvature of the viscosity curve is a maximum to be

$$x = \frac{\sqrt{\varphi_2 - \varphi_1} - \varphi_1}{\varphi_2 - \varphi_1}. \qquad (4)$$

Substituting this value in equation (3), one obtains the amount of curvature where the curvature is a maximum to be

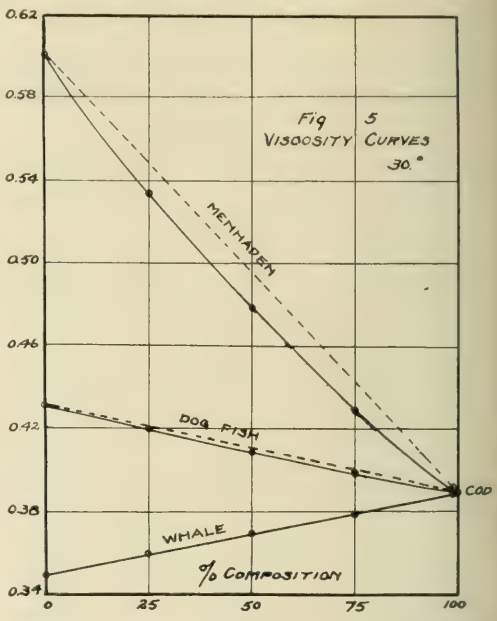
$$K = \sqrt{\frac{\varphi_2 - \varphi_1}{2}}. \qquad (5)$$

It follows, therefore, as a necessary consequence of the assumption that fluidities are additive that: 1. The curvature obtained by plotting viscosities is greatest when the difference between the fluidities, *i. e.*, $\varphi_2 - \varphi_1$, is large, and becomes zero when $\varphi_2 - \varphi_1 = 0$ [cp. equation (5)].

2. The curvature obtained by plotting viscosities must continually decrease as the concentration increases unless the square root of $\varphi_2 - \varphi_1$ is greater than φ_1, in which case the point of greatest curvature will be found at some positive concentration [cp. equation (4)].

3. Mathematically considered the curvature is dependent only upon the difference in the fluidities of the components, *i. e.*, $\varphi_2 - \varphi_1$ and not upon φ_1 [cp. equation (5)], but since we can only realize positive values of x, it follows that for a given value of $\varphi_2 - \varphi_1$ the curvature at any concentration will be greatest when φ_1 is very small.

That the curvature is greatest when the fluidities are quite unequal has already been noted by observers.[1] That the curvature is greatest when the viscosities are great has also been observed in the measurements of the viscosity of undercooled[1] and other very viscous liquids. It has caused some bewilderment, but we believe that the cause of this peculiarity has never before been given. The conclusion that the curvature is not uniform, is also clearly shown in the case of very viscous liquids. It is not shown very well by the curves which are given in this paper because the fluidities of the components are not sufficiently unequal.



In conclusion, it is possible that the fluidities and viscosities of oil mixtures *may* be simultaneously additive, but it seems to be a perfectly general rule that the fluidity is invariably a linear function of the composition so long as there is no marked action between the components.

I wish to express my gratitude to Dr. Eugene C. Bingham for valuable suggestions with regard to this investigation.

Laboratories of Richmond College, Richmond, Va., and U. S. Bureau of Fisheries, Woods Hole, Mass.

[1] Thorpe and Rodger, *J. Chem. Soc. London*, **71**, 361 (1896); Bingham, *Am. Chem. J.*, **35**, 195 (1906).

[1] Tammann, *Z. physik. Chem.*, **28**, 17 (1898).

COMPARATIVE VALUE OF IRRIGATED AND DRY-FARMING WHEAT FOR FLOUR PRODUCTION.

By Robert Stewart and C. T. Hirst.

Received Nov. 10, 1911.

The Chemical Department of the Utah Experiment Station has been conducting investigations during the past eight years regarding the milling, chemical and baking characteristics of different varieties of wheat grown under irrigated and dry-farming conditions. A great many varieties of wheat have been

vestigated, many of which were imported from ifferent sections of the country. The dry-farming arieties of wheat have been grown on the several xperimental dry farms, while the irrigated varieties ave been grown on the irrigated farm located in the ache Valley at Greenville.*

In 1908, a preliminary report of these investigations as published.[1] Some very important results were btained. It was found that the dry-farming wheats ere characterized by a low moisture and a high rotein content. The fact that dry-farming wheats ave a low moisture content is important. A dif- erence of one per cent. in moisture in a large con- gnment of wheat renders the wheat having the wer moisture content of higher intrinsic value. t was found that the protein content of the flour roduced from the durum varieties of wheat was 7.64 per cent. The protein content of the flour roduced from the common bread varieties of wheat as found to be 16.79 per cent., while the protein ontent of the flour produced from irrigated wheat as found to be 13.34 per cent., thus clearly indi- ating the higher protein content of the flour pro- uced from dry-farm wheats. It was found, however, hat in many cases the millers were unable to pro- uce good flour, from the baker's point of view, from he wheat they obtained from the farmers. These vestigations showed that this was due to two causes: rst, the most common variety of wheat grown in he state, the Gold Coin, contained the lowest pro- ein content of any of the varieties of wheat tested; econd, the farmers were not united on any one par- cular variety of wheat or any few varieties, but ach farmer was governed in his choice of the variety y his own personal inclinations, irrespective of the uality of wheat grown. The work clearly demon- rated the necessity of uniting on one or two varieties f wheat to be grown by the farmers for bread-making urposes, and it also clearly demonstrated the ne- essity of uniting upon the variety of wheat having high protein content, good chemical, milling and aking characteristics.

Since the publication of this bulletin, the work has been ontinued and the summarized results obtained by the hree-year investigations, 1907–8–9, are given herewith.

The summarized results for the yield of milling roducts of spring and winter dry-farming and irri- ated wheat during the years 1907–8–9 are recorded Table I.

ABLE I. SUMMARIZED RESULTS FOR YIELD OF MILLING PRODUCTS. RESULTS RECORDED AS PER CENT OF DRY WEIGHT.

	Tests	Weight 100 kernels,	Flour	Bran	Shorts	Error
rigated wheat, 25" water	10	4.008	68.08	23.39	8.52	-0.01
rigated wheat, 15" water	10	4.065	69.24	22.94	8.10	+0.28
o irrigation[2]	10	3.569	67.88	24.75	7.11	-0.26
inter dry-farm wheat	136	3.004	69.21	22.45	8.34	-0.03
ring dry-farm wheat	17	3.106	66.09	20.95	12.13	-0.83

[1] Stewart and Greaves, *Bull.* **103,** Utah Experiment Station.

[2] Wheat grown on *irrigated* land but receiving no irrigation water uring the growing season used as a check on application of varying mounts of water

The weight per 100 kernels of the irrigated wheat is greater than that of either the spring or winter dry-farming wheat. The yield of flour, bran and shorts shows nothing characteristic for the wheats grown under different conditions.

The results obtained for the moisture content of the flour, wheat, shorts, and bran are brought together in Table II.

TABLE II. SUMMARIZED RESULTS FOR MOISTURE IN FLOUR, WHEAT, SHORTS AND BRAN.

	Tests.	Flour.	Wheat	Shorts.	Bran
Irrigated wheat, 25 inches water....	10	10.41	8.46	9.41	8.54
Irrigated wheat, 15 inches water..	10	10.41	8.50	9.36	8.36
No irrigation.....	10	10.43	8.44	9.35	7.68
Winter dry-farm wheat.....	136	9.89	8.11	9.23	8.74
Spring dry-farm wheat.....	19	10.29	8.12	9.85	8.75

The moisture content is low in every case. The moisture content of the irrigated wheat is higher than that of the dry-farm wheat. The moisture content of the bran is practically the same as that of the wheat. The moisture content of the flour is about two per cent. higher than that of the wheat, while that of the shorts is about one per cent. higher than the wheat.

The results for the protein content of flour, wheat, shorts and bran are brought together in Table III.

TABLE III. SUMMARIZED RESULTS FOR PROTEIN IN FLOUR, WHEAT, SHORTS AND BRAN.

	Tests.	Flour.	Wheat.	Shorts.	Bran.
Irrigated wheat, 25 inches water .	10	12.63	14.00	16.40	18.87
Irrigated wheat, 15 inches water..	10	12.92	14.35	16.89	18.66
No irrigation.....	10	13.62	15.45	17.67	19.32
Winter dry-farm wheat.....	136	14.64	15.76	18.27	20.87
Spring dry-farm wheat.....	19	15.74	16.85	19.17	20.39

It is thus seen that the lowest protein content is found in the irrigated wheat. This has been previously observed at this experiment station.[1] The result obtained for the same varieties of wheat grown on the same land but receiving no irrigation water clearly indicates that the decrease in protein is due to the influence of the water and not to differences in varieties grown on irrigated and dry-farming land. This difference is also observed in the flour, bran and shorts. It is manifest to a greater degree, however, in the flour when the yield is taken into consideration. The difference in the amount of water applied to the plots receiving 25" and 15" of water is not sufficient to make any marked difference in the amount of protein in the wheat, flour, bran and shorts, although a slight difference is noted. The difference between the protein content of wheat which had received 25 inches of irrigation water and the spring dry-farm wheat is 2.85, the difference in the protein content of the flour produced from these wheats 3.11, while that of the shorts and bran is 2.77 and 1.42 per cent., respectively.

The summarized results obtained for the chemical composition of the flour produced from spring, winter and irrigated grain are recorded in Table IV.

[1] Widtsoe, *Bull.* **80,** Utah Experiment Station.

TABLE IV.—SUMMARIZED RESULTS FOR CHEMICAL COMPOSITION OF FLOUR.

	Tests.	Moisture.	Protein.	Moist gluten.	Dry gluten.	Ratio of wet to dry gluten.	Ash.
Irrigated wheat, 25" water.....	10	10.41	12.63	34.05	11.72	2.73:1	0.578
Irrigated wheat, 15" water.....	10	10.41	12.92	32.55	11.63	2.79:1	0.544
No irrigation.....	10	10.43	13.62	35.18	12.58	2.79:1	0.552
Winter dry-farm	136	9.89	14.64	40.14	14.14	2.85:1	0.529
Spring dry-farm	18	10.29	15.74	44.12	15.32	2.86:1	0.689

The flour produced from the winter dry-farm wheat has a slightly lower moisture content than the flour produced from the other kinds of wheat. The protein content of the flour produced from the wheat receiving the greatest amount of irrigation water is 3.11 per cent. lower than that produced from spring dry-farm wheat and 2.01 per cent. lower than that produced from dry-farm winter wheat. In case of the irrigated varieties of wheat, as the amount of water applied decreases, the protein content increases. The protein content of the flour produced from wheat which received no irrigation water is one per cent. greater than that produced from wheat receiving an application of 25 inches notwithstanding the fact that the seed wheat in both cases was the same and the non-irrigated wheat was grown on land which had been irrigated in previous years. The moist- and dry-gluten content of the flour produced from the irrigated wheat is considerably lower than that produced from either spring or winter dry-farm wheat.

The summarized results for the bread-making value of the flour produced from spring, winter dry-farm grains and the irrigated grains are recorded in Table V.

TABLE V.—SUMMARIZED RESULTS FOR BREAD-MAKING VALUE.

	No. of tests.	Cc. of water added.	Cc. of water retained.	Ratio of protein to vol. of water added.	Wt. of loaf.	Vol. of loaf.	Ratio of protein to vol. of loaf.
Irrigated wheat, 25" water.....	10	204	104	1:16.4	474	1605	1:127.1
Irrigated wheat, 15" water.....	10	185	105	1:14.3	475	1630	1:126.2
No irrigation.....	10	204	109	1:15.1	479	1655	1:121.5
Winter dry-farm.	108	195	104	1:13.3	474	1681	1:114.8
Spring dry-farm...	11	227	124	1:14.4	494	1841	1:117.0

The ratio of protein to volume of water added is narrower in case of the dry-farm grains. The volume of loaf made from dry-farm flour is slightly greater than that produced from irrigated flour. The ratio of protein to volume of loaf is narrower in the dry-farm flour than in the irrigated flour.

The investigations extending over a period of eight years clearly demonstrate the fact that the dry-farm grains in Utah are characterized by a low moisture content and a high protein content. They also clearly indicate that the protein content of the dry-farm wheats is higher than the protein content of the wheat on irrigated farms.

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THE INFLUENCE OF CARBON UPON NITRIFICATION.

By H. W. CLARK AND GEORGE O. ADAMS.

Received November 24, 1911.

During the past twenty-three years many experiments have been made at the Lawrence Experiment Station of the Massachusetts State Board of Health to determine the effect upon nitrification of an excess of a number of substances which may occur naturally in sewage or may at times find their way into it. The substances previously studied—the results in regard to which have been given in the various reports of the Station and especially in that of 1908—have been albumen, peptone, ammonium chloride and sodium carbonate, sulfuric acid, saltpeter, common salt, sugar, soap, urine, free oxygen, phenol, mercuric chloride, formalin, arsenic, naphthalene, sulfides, bleaching powder and copper sulfate. As stated in the conclusions of the summary of this work in the report of 1908, "the experiments illustrate the adaptability of the nitrifying body to the conditions imposed and establish another fundamental law of sewage purification that if nitrification is to continue in the presence of an excess of any substance, the filter must become slowly accustomed to the presence of that substance by application of it in gradually increasing amounts; that when once accustomed to considerable amounts of any substance, the process of nitrification will proceed unimpaired." It, of course, follows, however, that a great excess of any substance inimical to nitrification will prevent nitrification.

In the various investigations necessitated by the work of the State Board of Health, many experiments have been carried on in regard to the purification of mill wastes by filtration, many of these wastes containing large amounts of carbonaceous and small amounts of nitrogenous matter. It appeared from this work that at times with many of these wastes and at all times with some of them, good purification and a satisfactory effluent could be obtained when nitrates were not found in the effluents of the filters operated. Studies of this phenomenon appeared to show that whether nitrification occurred or not depended upon the relation of the amount of carbonaceous to nitrogenous matter present in the liquid or waste undergoing treatment; that is to say, nitrification could apparently proceed when the amount of nitrogen was represented by x and carbon by $10x$ but would be eliminated when the carbon was increased to 12 or $15x$. In order to make a thorough investigation of this subject, certain experimental filters were put into operation early in the year 1910 and the work has continued until the present time (September, 1911). The method has been to apply to the sand filters used, Lawrence sewage freed from matter in suspension to which has been added some body rich in carbon. Practically all the carbon and nitrogen applied has been in solution and by this means surface clogging and storage of organic matter in the filters has been prevented.

The bodies added to the different filters with the sewage, have been sugar, molasses, butyric acid, alcohol and filtered wool-scouring waste, and these

lters have been operated generally at a rate of 50,000 allons per acre daily. Careful and frequent determinaons of the relation between the carbon and the nitroen in the liquid applied have been made and also requent analyses of the effluent from each filter. he carbon values were calculated in the case of igar, alcohol and butyric acid, the composition of hich was known, and in the case of molasses the pproximate composition of which could be calcuted. The carbon content of the sewage used and f the filtered wool-scourings were calculated from ata obtained from other experiments upon the reation between loss on ignition and carbon.[1] While is not feasible to present in this article the full data regard to this investigation, the data in regard to he operation of several filters are given beyond to how the general method followed and the results btained. In all, twenty filters have been operated.

In the operation of the filters the carbon-containing odies have generally been added in slowly increasing mounts, while the nitrogen applied has been kept onstant. During the period when the ratio of carbon o nitrogen has remained low, active nitrification has ccurred in each filter and high nitrates have been resent in their effluents. When nitrification has been hecked by the large amounts of carbon applied, ach filter has been continued in operation long enough o prove conclusively that nitrification would not gain become active until the ratio of carbon to nitroen was considerably reduced and also long enough o prove that good purification continued without itrifying conditions in the filter. In all instances everal duplicate experiments with the same carbonaceous substance were made in order to prevent rors in our work and conclusions. Experiments ere also made showing that when nitrification had een checked, but not entirely stopped by the carbon, would be re-established by increasing the amount nitrogen in the liquid applied and keeping the rbon constant, this, of course, reducing the ratio carbon to nitrogen. It was also found that when mmonium chloride was added to the sewage, nitrication was not checked by carbonaceous bodies ven when added in very large amounts.

The main results of these experiments can be sumarized as follows:

When sugar was added in such amounts that the pplied liquid contained less than 50 parts of carbon, trification was stopped in three separate experients when the average carbon to nitrogen ratio as 13, 14 and 15. When the ratio was 11.6, 11.1 nd 11.0, nitrification was not seriously checked. hen nitrogen as NH_4Cl was added, nitrification ok place even when 200 parts of carbon as sugar as present in the applied liquid, and the ratio of rbon to nitrogen was 10.8. When molasses was dded with the sewage, nitrification was stopped hen the average carbon to nitrogen ratio was above , but active when this ratio was 10 and 11. With utyric acid, nitrification was not seriously impeded hen the average carbon to nitrogen ratio varied between 13 and 16, but was prevented when the carbon to nitrogen ratio was 27. When nitrogen as NH_4Cl was added with the butyric acid, nitrification took place even when acid equivalent to 200 parts carbon was present, the ratio of carbon to nitrogen being 14.0. With alcohol, nitrification was active when the average carbon to nitrogen ratio was 13 and 13.8, but was stopped when the average ratio was 15 and 16. When nitrogen as NH_4Cl was added with the alcohol, 400 parts of alcohol equal to 160 parts carbon could be applied to the filter and nitrification remain active, the carbon to nitrogen ratio under these conditions being 12.2. With filtered wool-scouring waste diluted with water, nitrification continued as long as the carbon to nitrogen ratio was below 14, the carbon running up to 350 parts per 100,000 but was stopped when the carbon to nitrogen ratio was increased to 17 by the addition of sugar.

Data in regard to three of these filters follow, and it will be noticed that even when nitrification ceased and the filters continued in operation, the amount of free and albuminoid ammonia present in the effluents of these filters was little, if any, greater than when nitrification was active. This occurred although the same amount of nitrogenous matter was being applied as when nitrification was active.

As stated in the beginning of this article, these results are similar to those obtained frequently with mill wastes and occasionally with domestic sewage and show that purification can take place in certain filters under the conditions imposed by the addition of large amounts of carbonaceous matter even although nitrification in the filter ceases. This purification without nitrification is due to certain bacteria which are active under conditions which prevent nitrification but cause chemical actions which break down organic matter and result in the setting free of carbon dioxide and nitrogen. It is distinctly different from the action sometimes occurring in contact filters where the nitrates formed do not appear in the effluent, as in such filters further oxidation of organic matter is accomplished within the filter by the use of the oxygen of these nitrates and their consequent reduction. The intense activity of the filter in changing

FILTER RECEIVING SEWAGE TO WHICH MOLASSES WAS ADDED. ANALYSES AT INTERVALS.

(Parts per 100,000.)

Free ammonia:					
Applied liquid.....	4.30	2.28	3.03	2.25	2.40
Effluent from filter.....	0.188	0.14	0.15	0.27	0.27
Albuminoid ammonia:					
Applied liquid.....	0.33	0.31	0.39	0.39	0.42
Effluent from filter....	0.026	0.036	0.04	0.042	0.046
Oxygen consumed:					
Applied liquid.....	12.14	16.99	19.10	23.80	23.80
Effluent from filter....	0.22	0.26	0.35	0:31	0.39
Kjeldahl nitrogen:					
Applied liquid.....	0.67	0.76	0.76	0.85	0.84
Nitrogen as nitrites:					
Effluent from filter....	0.0016	0.0014	0.0012	0.0004	0.0002
Nitrogen as nitrates:					
Effluent from filter....	2.52	2.18	2.01	0.84	0.10
Total carbon:					
Applied liquid.....	34.8	50.4	55.5	68.5	68.5
Ratio C/N:					
Applied liquid.....	8.3	16.1	17.0	24.4	24.3
Per cent. applied nitrogen in effluent.....	65.0	75.0	68.0	39.0	15.0

[1] THIS JOURNAL, 3, 738.

carbonaceous matter to the gaseous form, and its liberation and disappearance in this way, is strikingly shown by the oxygen-consumed results of the applied liquid and effluent. The loss of nitrogen by its liberation can be seen by the figures showing the percentage of that applied appearing in each effluent during different periods of operation of each filter.

FILTER RECEIVING SEWAGE TO WHICH BUTYRIC ACID WAS ADDED. ANALYSES AT INTERVALS.

(Parts per 100,000).

Free ammonia:							
Applied liquid	3.03	3.03	2.70	2.98	2.98	2.98	2.98
Effluent from filter	0.22	0.12	0.18	0.088	0.17	0.148	0.13
Albuminoid ammonia:							
Applied liquid	0.25	0.25	0.20	0.25	0.27	0.27	0.27
Effluent from filter	0.028	0.02	0.014	0.036	0.036	0.038	0.044
Oxygen consumed:							
Applied liquid	2.69	2.69	2.00	2.00	2.00	2.00	2.00
Effluent from filter	0.21	0.23	0.22	0.26	0.18	0.22	0.21
Kjeldahl nitrogen:							
Applied liquid	0.64	0.64	0.50	0.64	0.65	0.65	0.65
Nitrogen as nitrites							
Effluent from filter	0.004	0.002	0.0012	0.0006	0.0006	0.0006	0.0006
Nitrogen as nitrites:							
Effluent from filter	0.75	0.63	1.01	2.40	0.34	0.05	0.05
Total carbon							
Applied liquid	37.6	37.6	37.6	54.0	84.7	84.7	84.7
Ratio C:N:							
Applied liquid	12.0	12.0	13.8	17.5	27.4	27.4	27.4
Per cent. applied nitrogen in effluent	32.0	25.0	44.0	82.0	18.0	8.0	8.0

FILTER RECEIVING SEWAGE TO WHICH SUGAR WAS ADDED. ANALYSES AT INTERVALS.

(Parts per 100,000).

Free ammonia:							
Applied liquid	3.30	3.82	3.84	2.88	3.03	2.25	2.40
Effluent from filter	0.02	0.022	0.024	0.018	0.034	0.05	0.14
Albuminoid ammonia:							
Applied liquid	0.25	0.24	0.27	0.21	0.19	0.19	0.17
Effluent from filter	0.02	0.012	0.016	0.026	0.02	0.022	0.022
Oxygen consumed:							
Applied liquid	1.60	14.22	13.40	13.50	15.50	13.90	14.00
Effluent from filter	0.13	0.12	0.18	0.16	0.18	0.14	0.15
Kjeldahl nitrogen:							
Applied liquid	0.47	0.56	0.45	0.76	0.36	0.45	0.34
Nitrogen as nitrites:							
Effluent from filter	0.0040	0.0012	0.0004	0.0004	0.0004	0.0002	0.0002
Nitrogen as nitrates:							
Effluent from filter	3.11	1.39	2.65	2.86	1.43	0.67	0.04
Total carbon							
Applied liquid	4.7	40.7	39.2	41.6	45.5	46.0	43.3
Ratio C:N							
Applied liquid	1.5	11.0	10.9	14.7	15.9	20.0	18.4
Per cent. applied nitrogen in effluent	99.1	38.5	74.7	104.0	52.0	33.0	9.0

MILL WASTE FILTERS.

The following table shows the average results obtained during the past fifteen years of a number of filters operated with various mill wastes. The effluents from all these filters have been stable and usually clear and odorless. It will be noticed that where the ratio of carbon to nitrogen in the waste applied to the filter is around 10, there has been nitrification. In the case of the carpet mill waste, the first filter gave no nitrification because the carbon to nitrogen ratio was 16.1. This filter reduced the carbon to nitrogen ratio of the liquid to 9.0 so that when applied to a second filter, nitrification took place in the secondary filter.

	Applied waste. (Parts per 100,000.)			Effluent. (Parts per 100,000.)
Waste from:	Total Nitrogen	Approximate amount of carbon.	Ratio C/N.	Nitrogen as nitrates.
Dyeing cotton	0.58	41.6	71.0	0.02
Washing and dyeing cotton	0.76	21.8	28.6	0.01
Dyeing and finishing	0.57	11.4	20.0	0.00
Dyeing and finishing	0.27	5.2	19.2	0.07
Cotton batting	1.25	21.9	17.5	0.04
Carpet mill	2.24	3.6	16.1	0.05
Dyeing and finishing	1.80	26.8	14.9	0.10
Scouring and dyeing	0.91	10.8	11.9	0.37
Effluent from carpet mill filter No. 2	0.93	8.58	8.9	0.32
Binders' board	0.49	4.0	8.1	0.11
Shoddy mill	0.77	4.0	5.2	1.01
Tannery	4.65	19.4	4.0	3.63

LAWRENCE EXPERIMENT STATION,
MASS. BOARD OF HEALTH.

ACIDITY IN WHEAT FLOUR; ITS RELATION TO PHOSPHORUS AND TO OTHER CONSTITUENTS.

By C. O. SWANSON.

Received Jan. 25, 1912.

The investigation of the relation between chemical composition and the baking qualities of wheat flour is one of the major lines of investigation followed by the Chemical Department of the Kansas State Agricultural College Experiment Station. The chemical work in connection with this paper was done by Mr. John W. Calvin, Assistant Chemist, and Miss Leila Dunton, Fellow in Chemistry.

In our work on commercial flours it was noticed that there was an unmistakable relation between the percentages of acidity and the percentages of ash, amino compounds, total and water-soluble phosphorus. It was also noted that the acidity value and the related compounds depended to a large extent upon the method of milling. The presence of varying amounts of bran fiber or germ was more pronounced than any other factor.

To eliminate these factors of unknown influence it was decided to work on flours from different mill streams. The advantage of such flours was that their origin in relation to the different portions of the wheat kernel was better known. Also such flours would differ from each other to such an extent that small variations in the results due to experimental error would have less influence. In fact the differences on most of such flours are so great that the experimental error can in no way influence the main results. The description of the flours is given below. The wheat from which all these flours were made is also included. The serial numbers are the ones used throughout the discussion:

SERIAL NO.	DESCRIPTION OF SAMPLE, GIVING SOURCE.
389	Wheat from which the following twenty-six flours were made
390	Patent flour, seventy per cent.
391	Clear flour, twenty-seven per cent.
392	Low-grade flour, three per cent.
393	First break flour, part of the clear.
394	Second break flour, part of the clear
395	Third break flour, part of the clear.
396	Fourth break flour, part of the clear.
397	Fifth break flour, part of the clear.
398	First middlings flour, part of the patent.
399	Second middlings flour, part of the patent.
400	Third middlings flour, part of the patent.
401	Fourth middlings flour, part of the patent.

402	Fifth middlings flour, part of the patent.
403	Sixth middlings flour, part of the clear.
404	Seventh middlings flour, part of the clear.
405	First sizings flour, part of the patent.
406	Chunks flour, part of the patent.
407	Second sizings flour, part of the clear.
408	B middlings flour, part of the clear.
409	First tailings flour, part of the clear.
410	Second tailings flour, part of the clear.
411	Second low-grade flour, part of the low-grade.
412	Bran duster flour, part of the low-grade.
413	Ship duster flour, part of the low-grade.
414	Roll suction stock, part of the low-grade.
415	Stock going to fourth middlings from second sizings.

The chemical analyses of these flours for ash, protein, fat, acidity at 25° C. and 40° C., amino compounds, water-soluble phosphorus at 25° C. and 40° C. and total phosphorus are given in the accompanying table. The ash was determined by the calcium acetate method. The acidity was determined under two conditions: (1) the usual method, one-half hour extraction (room temperature about 25° C.) and (2) two hours' extraction at 40° C. That this latter method gives the maximum acidity was determined in a separate trial. The extracts from the acidity determinations were used in the determination of soluble phosphorus. The amino compounds were determined as follows: Eleven grams of flour were placed in a 600 cc. Erlenmeyer flask and 400 cc. of a 1% solution of sodium chloride added. The whole was thoroughly shaken and the shaking repeated every ten minutes for one hour. It was then allowed to settle for thirty minutes when a little over 200 cc. were filtered off. To exactly 200 cc. of the filtrate were added 20 cc. of a 10% solution of phosphotungstic acid. This was allowed to stand over night and then filtered. This filtrate was perfectly clear: 200 cc. of the filtrate were placed in a Kjeldahl flask, 5 cc. of sulphuric acid added, placed over a burner and the solution evaporated to 25 cc. More sulphuric acid was then added and the nitrogen determination finished in the regular way. The amino compounds were calculated as proteins. The percentage of the total phosphorus which is water-soluble was calculated and these figures are given in the last column.

ASH CONTENT.

The ash percentage increases in almost the same proportion as the flour contains fibrous branny material, or as the flours are taken from the portion of the wheat kernel next to the bran. The fifth break flour is highest in ash percentage, and the first break flour is next. The relatively high ash percentages of the first break flour is due to the incorporation of bran fibers when the flour is made, but in the fifth break the high ash content results from two causes: (1) the incorporation of bran fiber as in the first break and (2) the material in the wheat kernel next to the bran contains nore mineral matter than the interior of the kernel. This assumption is based on the composition of these mill streams in general. The middlings flours are lowest in ash. These are made from the interior portion of the kernel and by means of the purifiers they are very carefully freed from bran fibers. The flour from the chunks has a higher ash percentage than any of the streams which go into the patent flour. These chunks contain a relatively large amount of bran fiber and in grinding some of these fibers get into the flour. The ash content of bran and shorts is ten times that of flour. The percentage of ash furnishes a very good indication of the quality of the flour as far as that is related to the method of milling.

ACIDITY.

The acidity values, at 40°, two hours' extraction, show very clearly what portion of the wheat kernel the flour comes from.

As all these flours were made from the same wheat the effect of the unsound grain is eliminated. The presence of bran fiber, germ, or portions of the wheat kernel next to the bran, will largely influence the acidity values, probably more than unsoundness.

AMINO COMPOUNDS.

The amino compounds vary almost identically as the acidity and the same factors which influence the acidity also influence the percentage of amino compounds.

PHOSPHORUS.

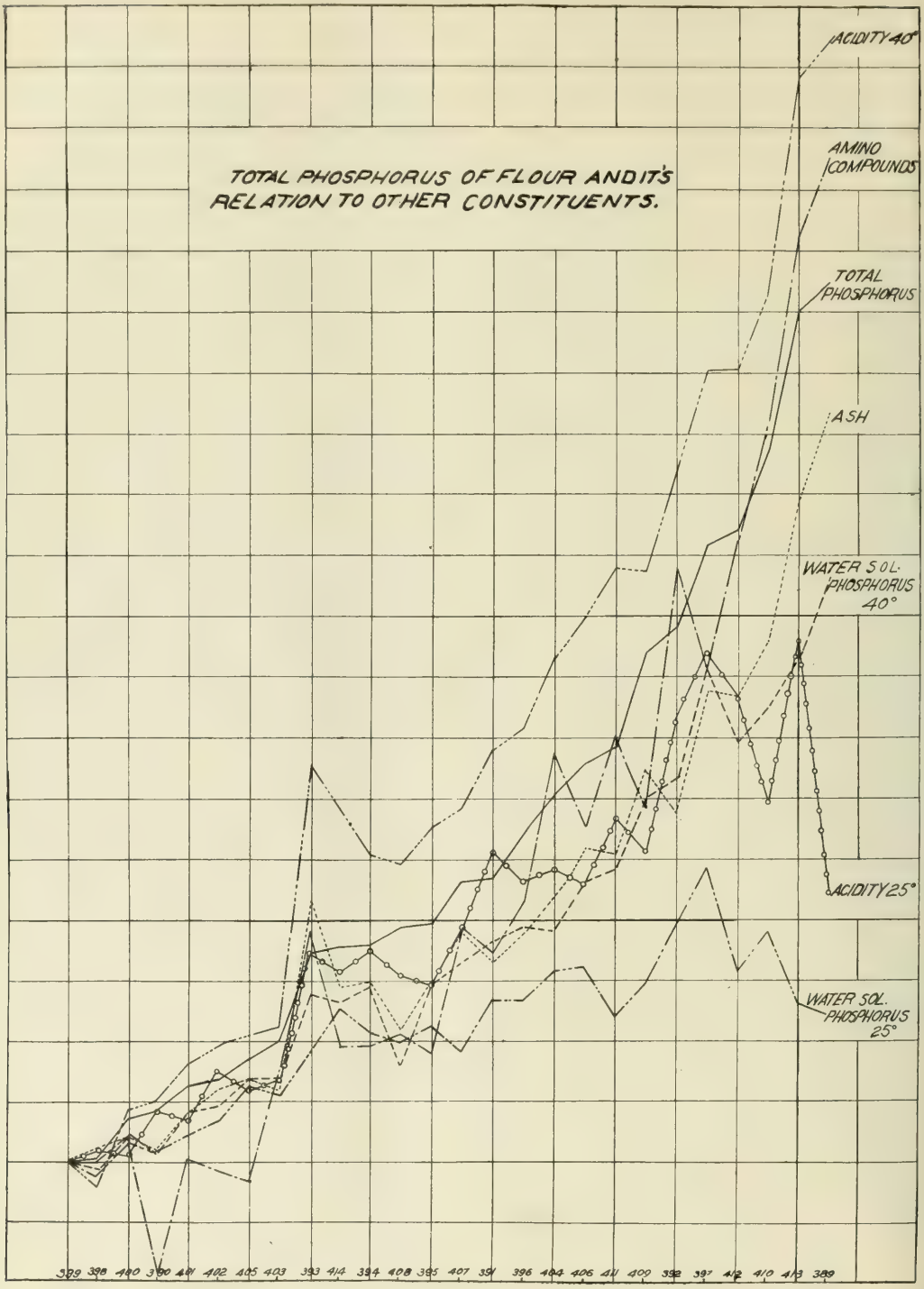
The total and water-soluble phosphorus show the same variations as the acidity and the amino compounds in relation to the portion of the wheat kernel from which the flour is taken.

The water-soluble phosphorus content, obtained by both methods of determination, varies with the total phosphorus, but not in the same proportion. The phosphorus soluble at 40° C., two hours' extraction, increases in a larger ratio in the lower mill streams than the phosphorus soluble at 25° C., half an hour's extraction.

The first middlings flour has the lowest percentage of water-soluble phosphorus followed closely by the patent flour and the second and third middlings. The amount of water-soluble phosphorus in the middlings increases as the number of designations of reduction increases. This statement is also true of the break flours. In all the lower streams, the percentage of water-soluble phosphorus is high as compared with the middlings flours.

The baking tests, made by Miss Dunton, showed clearly that the percentage of water-soluble phosphorus has a distinct influence on the total expansion and fermentation period. These phosphates, no doubt, have a very intimate relation to the gluten quality, and experiments are now in progress which we hope will throw some light on the problem.

A study of the accompanying table will show that there is an unmistakable relation between the acidity, the amino compounds and the phosphorus, both the total and the water-soluble. There is also an apparent relation between the ash and acidity. That the total phosphorus should show a relation to the acidity follows from the fact that it includes the soluble phosphates and the total and the soluble bear a more or less definite relation to each other. The larger


TOTAL PHOSPHORUS OF FLOUR AND IT'S RELATION TO OTHER CONSTITUENTS.
ACIDITY 40°
AMINO COMPOUNDS
TOTAL PHOSPHORUS
ASH
WATER SOL. PHOSPHORUS 40°
ACIDITY 25°
WATER SOL. PHOSPHORUS 25°
399 398 400 390 401 402 405 403 393 414 394 408 395 407 391 396 404 406 411 409 392 397 412 410 413 389

part of the phosphorus in the flour extract is probably in the form of phosphates of potassium. There are also smaller amounts of the phosphates of magnesium and calcium, the former being about four times as abundant as the latter, reasoning from the composition of wheat ash. The acid phosphates of magnesium are very slightly soluble in water. While monocalcium phosphate is soluble in water, the possible amount of this salt in the flour is very small. Reasoning from the different amount of inorganic elements present in the flour, much the larger part of the soluble phosphorus obtained in the extract water during extraction may easily change this condition.

In the following discussion, the figures for 70 per cent. patent flour, treatment at 40° C. two hours, are taken. The percentage acidity is 0.130. This corresponds to 2.88 cc. $N/20$, or 0.0081 g. KOH for 10 g. of flour. The per cent. of water-soluble phosphorus in an extract from the same amount of flour and obtained under the same condition is 0.028. This would correspond to 0.0028 g. of phosphorus; that is, the water extract which requires 0.0081 g. of KOH to neutralize the acidity contains 0.0028 g. of soluble

Chemical Composition of Flour from Different Mill Streams. Moisture-Free Percentages.

			Acidity.			Phosphorus.			
No.	Mill stream.	Ash.	25°.	40°.	Amino comp.	Water sol. at 25°.	Water sol. at 40°.	Total.	Per cent. of water soluble at 40°.
389	Wheat	1.93	0.156	0.478	0.530	0.066	0.218	0.482	51.73
390	Patent 70 per cent.	0.52	0.074	0.130	0.162	0.021	0.028	0.110	29.25
391	Clear 27–27½ per cent.	0.83	0.170	0.245	0.270	0.071	0.098	0.187	59.64
392	Low grade 2½–3 per cent.	1.08	0.215	0.339	0.396	0.097	0.152	0.269	64.01
393	First break	0.93	0.136	0.239	0.276	0.053	0.082	0.162	57.79
394	Second break	0.80	0.137	0.211	0.239	0.060	0.083	0.165	57.45
395	Third break	0.80	0.126	0.220	0.237	0.062	0.084	0.172	55.74
396	Fourth break	0.88	0.160	0.252	0.266	0.071	0.103	0.204	78.34
397	Fifth break	1.28	0.235	0.370	0.363	0.114	0.187	0.296	72.29
398	First middlings	0.52	0.071	0.101	0.195	0.017	0.023	0.094	27.43
399	Second middlings	0.50	0.067	0.109	0.200	0.017	0.025	0.093	30.55
400	Third middlings	0.54	0.069	0.125	0.206	0.026	0.033	0.107	34.93
401	Fourth middlings	0.58	0.081	0.142	0.201	0.026	0.042	0.118	40.26
402	Fifth middlings	0.62	0.067	0.148	0.217	0.031	0.044	0.120	41.58
403	Sixth middlings	0.62	0.094	0.164	0.229	0.039	0.053	0.133	44.89
404	Seventh middlings	0.95	0.164	0.275	0.335	0.080	0.102	0.215	53.69
405	First sizings	0.64	0.091	0.161	0.194	0.042	0.051	0.127	46.21
406	Chunks	1.02	0.159	0.289	0.312	0.082	0.118	0.225	59.74
407	Second sizings	0.88	0.145	0.236	0.278	0.054	0.091	0.186	56.02
408	B. middlings	0.72	0.129	0.208	0.243	0.057	0.077	0.171	25.47
409	First tailings	1.15	0.170	0.304	0.317	0.076	0.145	0.261	63.16
410	Second tailings	1.36	0.186	0.395	0.444	0.094	0.175	0.327	60.68
411	Second low grade	1.01	0.181	0.305	0.340	0.065	0.122	0.230	59.51
412	Bran duster flour	1.27	0.220	0.370	0.404	0.080	0.161	0.301	59.91
413	Ship duster flour	1.58	0.239	0.466	0.505	0.070	0.191	0.373	57.53
414	Roll suction stock	0.79	0.130	0.467	0.239	0.068	0.078	0.164	53.72
415	Middlings from second sizings	0.46	0.065	0.133	0.076	0.023	0.079	0.113	79.20

is in the form of the phosphates of potassium. All the phosphates of potassium are more or less soluble in water. Some are soluble in alcohol while others are not. Orthopotassium phosphate is slightly soluble in cold water and the solubility increases at a higher temperature. Monopotassium phosphate and dipotassium phosphate are both soluble in cold water; the former gives a solution acid in reaction, while the latter gives a solution alkaline in reaction. It thus becomes evident why a soluble phosphate obtained from a flour will influence the acidity test. The effect of varying temperature on solubility of the different phosphates of potassium partly explains why the percentages are higher at 40° C.

Whether or not these phosphates are present as such in the flour or produced by the hydrolytic action of the water in the process of extraction is immaterial as far as they influence the acidity value. It is this water extract that is used for the determination of acidity, and in which the acid phosphates would be found. It may be that the greater part of the phosphorus in the flour is present in the organic form. Determinations made in this laboratory seem to point that way, but the hydrolytic action of the phosphorus in the form of acid phosphates. Assuming that this phosphorus is in the form of monopotassium phosphate, there would be 0.0123 g. of this salt.

Assuming the chemical reaction to take place in accordance with the following equation,

$$KOH + KH_2PO_4 = K_2HPO_4 + H_2O,$$

we have the following proportion:

$$56.1 : 136.1 : : 0.0081 : X = 0.0196$$

This means that it would take 0.0196 g. of monopotassium phosphate to be neutralized by the 0.0081 g. of KOH, while according to the determinations there was only 0.0123 g. of this salt present as calculated from the amount of soluble phosphorus. If we assume the above reaction to take place this amount of monopotassium phosphate would require only 0.0051 gram of KOH for its neutralization. The difference between 0.0081 and 0.0051 or 0.003 g. of KOH would be neutralized by some other compounds. That these compounds are the amino acids is evident from the close relation between the acidity value and the amino compounds. The close relation between the ash percentages and the acidity is due

to the greater content of phosphorus in the samples which are high in ash.

GRAPHIC PRESENTATION OF THE RELATION BETWEEN PHOSPHORUS AND OTHER CONSTITUENTS IN MILLSTREAM FLOURS.

The figures for total phosphorus given in the table of analyses were arranged in an ascending series and the figures for the other constituents placed in parallel columns. These figures were then plotted on cross-section paper with the results shown in the accompanying plate. To bring the curves near each other on the plate, the figures for each constituent of No. 399, second middling flour, were reduced by addition and subtraction to the same value as the figure for total phosphorus. The corresponding figures for the constituents of all the flours were treated by the same factors as were used in changing the numerical values for the constituents on No. 399. This does not change the form of the curve but the relative position is changed. Unless some such method were used, it would not be possible to show all these curves on one plate. But, it should be borne in mind that on account of these calculations, the fact that one curve is above another does not mean that the absolute value is greater. The plate shows only the relation of the curves to each other, not the relative magnitude of the constituents represented.

THE CHEMISTRY OF ANAESTHETICS, IV: CHLOROFORM.

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Received December 13, 1911.

(Continued from the March No.)

V. The Physical Constants of Chloroform.

1. SPECIFIC GRAVITY.

A. The earliest determinations of the density of chloroform were made in 1832 by Liebig,[1] who reported the constant 1.485 at 15°, and by Guthrie,[2] who found the value to be 1.486 at 15.5°. Later (1849), Soubeiran and Mialhe[3] obtained a purer preparation, as shown by their density determination, 1.4905 at 15°. Up to 1849, however, the best commercial chloroform possessed a specific gravity of 1.480, which was considered a guarantee of its purity. Gregory[4] found that chloroform of the density 1.480, when once treated with sulphuric acid, which destroyed the "oils," might be obtained, after removing the "sulphurous acid," of the density of 1.500 at 15.5°. This value he took as the true specific gravity of chloroform. Wilson was unable to obtain chloroform of a density higher than 1.498; but Gregory considered his chloroform impure, and stated that every sample, whether originally of 1.480, 1.490, or 1.497, when purified by means of sulphuric acid and manganese dioxide, acquired the density which he regarded as true, *viz.*, 1.500 at 15.5°.

Schiff,[1] in 1858, reported that chloroform possesses a density of 1.5066 at 15°; this high result was probably attributable to the method of purification which he employed. In 1865, Hager stated that "pure" chloroform possesses a density of 1.494–1.495 at 15°.[2] Swan[3] reported that his determinations showed 1.493–1.497; but these results, like those of Soubeiran and Mialhe, and Gregory, were due to the fact than no special pains were taken to free the chloroform from alcohol.

The determinations of Thorpe[4] were made on chloroform which had been carefully purified,[5] and undoubtedly represent great accuracy. Thorpe found the density to be 1.52657 at 0°/4°, with which value the recent determinations of Timmermans,[6] 1.52633–7 for d_4^0, are in accord. A summarization of the various determinations of the specific gravity of chloroform is given in Table I.

TABLE I.—VARIOUS DETERMINATIONS OF THE SPECIFIC GRAVITY OF CHLOROFORM.

0°.	11.8°.	12°.	15°.	15.5°.	16.5°.	17°.	18°.
1.52523[7]	1.5039[9]	1.496[10]	1.485[12]	1.500[23]	1.472[24]	1.491[25]	1.482[27]
1.52657[8]		1.512[11]	1.4946[13]			1.507[26]	
			1.4905[11]				
			1.4976[15]				
			1.5066[16]				
			1.5107[17]				
			1.4989[18]				
			1.4980[19]				
			1.500[20]				
			1.50027[21]				
			1.50085[22]				

18.58°.	25°.	29°.	35.86°.	60.8°.	61.2°.	63°.
1.48978[28]	1.48432[29]	1.49089[30]	1.45695[31]	1.4081[32]	1.40877[33]	1.3954[34]
	1.48492[29]					1.4018[35]
						1.40814[36]

[1] *Ann.*, **1**, 199.

[2] *Am. J. Sci.*, [1] **22**, 105.

[3] *Jahresber.*, **2**, 408. The densities given were calculated from the values reported.

[4] *Pharm. J.*, **9**, 580.

[1] *Ann.*, **107**, 63.

[2] *Kommentar*, **439**. The requirement of the *Pharmacopoea Borussica* at this time was 1.492–1.496. "English Chloroform," already referred to, possessed a density of 1.485.

[3] *Phil. Mag.*, [3] **33**, 38.

[4] *Trans. Chem. Soc.*, **37**, 196.

[5] The method employed has already been described under *Purification*.

[6] *Bull. soc. belg. chim.*, **24**, 244.

[7] Pierre, *Compt. rend.*, **27**, 213.

[8] Thorpe, *J. Chem. Soc.*, **37**, 371. Referred to water at 4°.

[9] Schiff, *Gazz. chim. ital.*, **13**, 177. Water at 4°.

[10] Soubeiran and Mialhe, *Jahresber.*, **2**, 408. Not free from alcohol

[11] Schiff, *Ann.*, **107**, 63.

[12] Calculated from [21].

[13] Calculated from [19].

[14] Calculated from [4].

[15] Calculated from [1].

[16] Calculated from [5].

[17] Calculated from [20].

[18] Calculated from [2].

[19] Calculated from [3].

[20] Remys, *J. Chem. Soc.*, **13**, 439.

[21] Perkin, *J. prakt. Chem.*, [2] **32**, 523. Water at 15°.

[22] Perkin, *Ibid.* Water at 15°

[23] Gregory, *Jahresber.*, **3**, 454. Not free from alcohol.

[24] Geuther.

[25] Regnault, *Ann. chim. phys.*, [2] **71**, 381.

[26] Flückiger, *Z. anal. Chem.*, **5**, 302. Water at 17°.

[27] Liebig, *Ann.*, **1**, 199.

[28] Drecker, *Pogg. Ann.*, [2] **20**, 870.

[29] Perkin, *Loc. cit.* Water at 25°.

[30] Nasini, *Gazz. chim. ital.*, **13**, 135.

[31] Drecker, *Loc. cit.*

[32] Schiff, *Ber.*, **15**, 2972.

[33] Thorpe, *Loc. cit.*

[34] Ramsay, *J. Chem. Soc.*, **35**, 463.

[35] Schiff, *Ber.*, **14**, 2763.

[36] Schiff, *Ibid.*

In the course of their investigation of the decomposition of chloroform, the authors had occasion to prepare chloroform which they regard as absolutely pure.[1] This possessed a density of 1.49887 at 15°/4° (average of six determinations), a result in close agreement with the values of Thorpe and Timmermans, and which we consider to be the correct specific gravity at this temperature.

B. The anaesthetic chloroform on the American market varies in specific gravity from 1.4730–1.4827 at 25°/25°, usually in close proximity to 1.476, the minimum density permitted by the *Pharmacopoeia*. The samples of chloroform of German manufacture examined by the authors varied in specific gravity from 1.487–1.492 at 15°/15°, although one sample possessed a density of 1.497 at this temperature. Since the correct specific gravity of chloroform is 1.49887 at 15°/4°. those authorities requiring chloroform of a lower density—that is, anaesthetic chloroform—allow the addition of alcohol, and consequently the presence of small amounts of water; the permissible addition usually varies from 0.5–1 per cent.[2]

The specific gravities of the chloroforms recognized as official by the pharmacopoeias of various countries are given in Table II.[3]

TABLE II.—DENSITIES ACCORDING TO VARIOUS PHARMACOPOEIAS.

1.480	1.489	1.490	1.497	1.498	1.500	1.485–1.489	1.485–1.490
Spain[4] Portugal[5] Mexico[6]	Switzerland[7]	Greece[8]	Chili[9]	France[10]	Roumania[11]	Germany[12] Denmark[13] Hungary[14] Norway[15] Sweden[16] Finland[17]	Belgium[18]

1.485–1.495	1.485–1.500	1.490–1.493	1.490–1.495	1.498–1.500	1.499–1.500	Not below 1.476 at 25°
Japan[19]	Austria[20]	Italy[21]	Great Britain[22]	Holland[23]	Russia[24]	United States[25]

[1] The method of purification used was as follows: 500 cc. of chloroform containing 0.7 per cent. of absolute ethyl alcohol and 0.04 per cent. of water, but otherwise pure, were agitated with 1 liter of water repeatedly throughout one day; the water was then removed, and the treatment was repeated twice in the dark. The separated chloroform was then shaken with 500 cc. of water throughout one day, and finally with two successive portions of 250 cc. It was then dried over fused calcium chloride, and afterwards agitated with 1/5th its volume of concentrated sulphuric acid, when to our surprise—for the chloroform had originally afforded no coloration with sulphuric acid, and the process of purification had so far been conducted in the dark—the acid assumed a yellow color. It was therefore found necessary to continue the treatment with sulphuric acid, until the chloroform failed to color it, to accomplish which three successive treatments were necessary. The chloroform was then tested for the presence of alcohol by the chromic acid, iodine, iodoform, and fuchsine tests (see *Alcohol*), and was found to be alcohol-free. It was accordingly agitated with 75 g. of anhydrous sodium carbonate during three days, separated by filtration, and 400 cc. were fractionated. The chloroform almost completely distilled over between 61.2° and 61.8°, and all above 62° (about 5 cc.) was eliminated. After refractionation, the chloroform was carefully examined and was found to be free from alcohol, water, acetaldehyde, and decomposition products; it gave no coloration with formalin-sulphuric acid.

[2] See *Alcohol*.

[3] No reference is made in the table to chloroform intended for industrial purposes.

[4] *Farmacopea Oficial Española*, **1905**, p. 198.

[5] Hirsch's "Universal-Pharmakopöe," **1**, 162 (1902).

[6] At 18°. *Nueva Farmacopea Mexicana*, **1904**, p. 497.

[7] *Pharmacopoea Helvetica*, **1907**, p. 101. Formerly 1.485–1.490.

[8] Hirsch, *Loc. cit.*

[9] *Farmacopea Chilena*, **1886**, p. 147.

The chloroform constants according to various editions of the *United States Pharmacopoeia* are as follows:

Date.	Density at 15°.	Boiling point.
1851	1.49	142° F.
1869	1.490–1.494	140° F.
1873	1.480	142° F.
1882	1.485–1.490	60°–61° C.
1893	Not below 1.490	60°–61° C.

C. Regnauld[1] maintained that the specific gravity of chloroform is hardly a criterion of its purity, owing to conflicting results; but this statement was based upon the results of an examination of various samples of chloroform at a period prior to the adoption of improved methods of manufacture and purification, and before the formulation and recognition of more stringent pharmacopoeial standards. Specific gravity should not be regarded by any means as the *sole* criterion of purity; but the constant is indicative of the strength and, although to less degree, the purity of anaesthetic chloroform, and should always be determined.[2] For this purpose the pyknometer should be employed[3] and the determination should be made preferably at 15°. The Mohr-Westphal balance will serve to give a rapid approximate result, but should not be depended upon where any considerable degree of accuracy is desired. Chloroform is quite sensitive to temperature variations, but owing to the fact that it is considerably less volatile than ether, as well as comparatively non-hygroscopic, the determination of its density does not present such difficulties as are often encountered in the case of ether.

2. BOILING POINT.

A. The boiling point of chloroform was first deter-

[10] *Codex Medicamentarius Gallicus*, **1908**, p. 148. The specific gravity given is that specified for "Chloroforme Officinal;" it is stated that "Chloroformium Depuratum" possesses a density of 1.495–1.500, depending on its purity.

[11] Hirsch, *Loc. cit.*

[12] *Pharmacopoea Germanica*, **1900**, p. 86; *Deutsches Arzneibuch*, **1910**, p. 118. It is of interest to note here that in 1865 the *Ph. Hessen* specified chloroform of the density 1.515 at 17.5°, and that the *Ph. Hannover* stated the density 1.48.

[13] *Pharmacopoea Danica*, **1907**, p. 94.

[14] *Pharmacopoea Hungarica*, **1909**, p. 73.

[15] Hirsch, *Loc. cit.* The *Pharmacopoea Norvegica*, **1879**, p. 61, specifies 1.485–1.493.

[16] *Pharmacopoea Svecica*, **1908**, p. 76.

[17] *Pharmacopoea Fennica*, **1885**, p. 48.

[18] *Pharmacopoea Belgica*, **1906**, p. 65. Formerly 1.491 at 17°.

[19] *Pharmacopoeia of Japan*, third edition, **1907**, p. 84.

[20] *Pharmacopoea Austriaca*, **1889**, p. 61. Squire gives 1.485–1.490.

[21] Squire's *Companion to the British Pharmacopoeia*, **1908**, p. 373. The *Farmacopea Italiana*, fourth edition, p. 1357, gives 1.49.

[22] *British Pharmacopoeia*, **1908**, p. 75. In 1868 a *Pharmacopoeia of India* was issued; in this work the density 1.49 was specified (p. 266).

[23] *Pharmacopoea Nederlandica*, **1905**, p. 90. The density given is that of the "Chloroformum ad narcosin" (chloral chloroform); "Chloroformum" (0.6–1.0 per cent. alcohol) is stated to possess a specific gravity of 1.485–1.489.

[24] Squire, *Loc. cit.* The *Pharmacopoea Russica*, **1880**, p. 110, gave 1.485–1.490. Hirsch (*Loc. cit.*) gives 1.485–1.489.

[25] *Pharmacopoeia of the United States of America*, 8th revision, p. 99.

[1] *J. pharm. chim.*, [4] **29**, 402.

[2] As a rule, the specific-gravity determination is indicative of the amount of alcohol in chloroform, although such chloroform must, of course, always be examined for the presence of impurities and decomposition products. These points will be discussed in the course of the paper, under the various probable impurities. On the effect of alcohol on the density of chloroform, see *Alcohol*.

[3] The form of pyknometer designed by Perkin (*J. prakt. Chem., N. F.*, **31**, 486) is very suitable, although we have found the Sprengel pyknometer satisfactory.

mined by Liebig[1] who found the constant 60.8° C., and by Guthrie,[2] who, although he obtained a purified product of practically the same density as that of Liebig, stated that "absolutely pure chloric ether" boils at 74.4° C., a result doubtless attributable to the method of determination employed. Pierre,[3] in 1851, also obtained a high result—63.5° at 772.52 mm. due, for the most part, to the impure chloroform employed in the determinations he conducted. In 1854, the boiling point of chloroform was given as 62°,[4] the same constant being given in 1861;[5] and although the determination of Regnault,[6] namely, 60.16° at 760 mm., had received recognition three years previously, we find it stated in 1866 that the boiling point of chloroform is 63°.[7] The constant found by Regnault appears to have been widely accepted as late as 1880; but the mean determination of Thorpe.[8] 61.2°, later supplanted it and is now given by various authorities.[9] The mean of the maximum (61.21°) and minimum (61.19°) of the recent accurate determinations of Timmermans[10] is 61.20°, the correct boiling point of pure chloroform.[11]

Other determinations of the boiling point of chloroform are as follows:

Year.	Observer.	Temperature.
1883.....	Schiff[12]	60.9° at 754.3 mm.
1884.....	Perkin[13]	62.0° at 760 mm.
1885.....	Bauer[14]	61.0° at 760 mm.
1899.....	Thayer[15]	61.6° at 760 mm.
		61.64° at 760 mm.
1899.....	Petit[16]	61.97° at 760 mm.
1904.....	Wade and Finnemore[17]	61.15° at 760 mm.

B. The boiling points of the chloroforms recognized as official by the various pharmacopoeias are given in Table III. In general, it may be said that no specific directions are given for the determinations of the constant,[18] and that the influence of the variables (alcohol and water, in particular) on the boiling point has received very little attention.

C. Opinions are divided as to the value of the boiling-point determination as a criterion of the purity of anaesthetic chloroform. It has been stated that it is a valuable indication of the purity, since the presence of 0.5 per cent. of alcohol reduces the boiling point to "59.8° or 60°" and owing to the fact that a boiling point higher than "61°" indicates the presence of amyl or butyl compounds,[1] while Arzberger[2] has pointed out that in the determination of the boiling point of chloroform it is important that the distillation be continued until the last drops have been vaporized and that a perceptible rise of temperature at this point indicates the presence of water. Brown, however, expressed the opinion that the determination of the boiling point has little value so far as estimating the impurities of commercial chloroform is concerned.[3] Others have obtained anomalous results in attempting to determine the constant.[4]

Table III.—Boiling Points According to the Various Pharmacopoeias.

59.5–61.5°.	60°.	60.8°.	61°.
Sweden[5]	Italy[6]	Spain[7]	Mexico[11]
		France[8]	Greece[12]
		Chili[9]	
		Roumania[10]	

60–61°.	60–62°.	61.3°.	61–62°.
United States[13]	Great Britain[15]	Holland[24]	Hungary[25]
Russia[14]	Germany[16]		
	Austria[17]		
	Switzerland[18]		
	Belgium[19]		
	Denmark[20]		
	Norway[21]		
	Japan[22]		
	Finland[23]		

[1] *Loc. cit.* The same value was later reported by Regnault (*J. pharm. chim.*, [4] **29**, 402.)

[2] *Loc. cit.*

[3] *Ann. chim. phys.*, [3] **33**, 199.

[4] Limprecht, "Lehrbuch der Organischen Chemie," p. 161.

[5] Kolbe, "Ausfuhrliches Lehrbuch der Organischen Chemie," Vol. I, p. 589.

[6] *Compt. rend.*, **39**, 301, 345, 397; see particularly, *Jahresber.*, **1863**, 70.

[7] Sharples, "Chemical Tables," p. 69.

[8] *Trans. Chem. Soc.*, **37**, 196.

[9] *E. g.*, Beilstein; Landolt-Börnstein.

[10] *Bull. soc. belg. chim.*, **24**, 244. Timmermans found that the variation dt/dp of the b. p. for 10 mm. pressure is 0.36°.

[11] The absolutely pure chloroform prepared by the authors possessed this boiling point, as determined by the arrangement of Berthelot and corrected to normal.

[12] *Ann.*, **220**, 95.

[13] *Trans. Chem. Soc.*, **45**, 530.

[14] *Ann.*, **229**, 163.

[15] *J. Phys. Chem.*, **3**, 37.

[16] *Ibid.*, **3**, 351. Petit purified the chloroform used by washing it twelve times with water, then shaking it with a concentrated solution of calcium chloride. The chloroform was then fractioned through a Hempel column, and the part kept was that distilling over between 60° and 60.3° at 741 mm. The corrected boiling point of this fraction was found to be 61.97°, much higher than recently reported. The impurity causing this high boiling point was not discovered by Petit.

[17] *Trans. Chem. Soc.*, **85**, 946.

[18] Exceptions are the *Pharmacopea Nederlandica*, 1905 [*J. pharm. chim.*, **23**, 479 (1906); *Chem. and Drug.*, **69**, 828] and the *Pharmacopea Austriaca*, 8th revision, p. 25.

[1] Allen, "Commercial Organic Analysis," Vol. I, 236. Cf. Hager, *Pharm. Z. Russland*, September, **1869**.

[2] *Pharm. Ztg.*, **51**, 321.

[3] *Pharm. J.*, March 19, 1892.

[4] For example, Werner (*Archiv. Pharm.*, [iii] **12**, 481) stated that chloroform boils over a naked flame at 62–63°, but that it does not boil below 64° on a water bath and often not until a temperature of 66° has been reached. In the latter case, Werner found that it was difficult to determine whether the liquid was boiling, as the surface showed no signs of ebullition. By immersing a piece of string in the chloroform to be distilled Werner found the difficulty was removed(!).

[5] *Pharmacopoea Svecica*, **1908**, p. 76

[6] *Farmacopea Italiana*, fourth edition, p. 1357. Hirsch gives 61–62°.

[7] *Farmacopoea Oficial Espanola*, **1905**, p. 198.

[8] *Codex Medicamentarius Gallicus*, **1908**, p. 148. The boiling point given is that specified for "Chloroforme Officinal," or "Chloroformum pronarcosi;" the boiling point of "Chloroformium depuratum" is stated to be 61°.

[9] *Farmacopoea Chilena*, **1886**, p. 147.

[10] Hirsch's *Universal-Pharmakopöe*, **1**, 162 (1902).

[11] *Nueva Farmacopea Mexicana*, **1904**, p. 477. At 76 cm. pressure.

[12] Hirsch, *Loc. cit.*

[13] *Pharmacopoeia of the United States of America*, 8th revision, p. 99.

[14] *Pharmacopoea Russica*, **1880**, p. 110. This is the latest edition of the work we have seen, but Hirsch (*Loc. cit.*) gives 60–62°.

[15] *British Pharmacopoeia*, **1908**, p. 75.

[16] *Pharmacopoea Germanica*, **1900**, p. 86; *Deutsches Arzneibuch*, **1910**, p. 118.

[17] *Pharmacopoea Austriaca*, **1889**, p. 61.

[18] *Pharmacopoea Helvetica*, **1907**, p. 101.

[19] *Pharmacopoea Belgica*, **1906**, p. 65.

[20] *Pharmacopoea Danica*, **1907**, p. 94.

[21] Hirsch (*Loc. cit.*). The *Pharmacopoea Norvegica*, **1879**, p. 61, gives 60–63°.

[22] *Pharmacopoeia of Japan*, third edition, **1907**, p. 84.

[23] *Pharmacopoea Fennica*, **1885**, p. 48.

[24] *Pharmacopoea Nederlandica*, **1905**, p. 90. The value given is that specified for "Chloroformum ad narcosin" (chloral chloroform); "Chloroformum" containing 0.6–1.0 per cent. of alcohol is stated to boil at 60° (62 cm.).

[25] *Pharmacopoea Hungarica*, **1909**, p. 73. In this place it may be noted that the *Pharmacopoea Croatico-Slavonica*, **1888**, p. 163, specifies "Chloroformium e chloralo," boiling point 60–61°.

While it is true that in the ordinary method of fractionation, any impurities decomposable by sulphuric acid and chlorinated decomposition products are concentrated in the residue and may then be recognized,[1] in the opinion of the authors the boiling-point determination is not a criterion of the purity of anaesthetic chloroform, unless either (*a*) pure chloroform—that is, absolute chloroform—is specified, or (*b*) the amount of alcohol (and water) added is definitely fixed and no range of addition, such as 0.4–1.0 per cent., is permitted. In any case, definite directions should be given in order that a standard method of determination would be employed.

When anaesthetic chloroform is distilled, the temperature rises immediately to about 55.5°, at which temperature water passed over with part of the alcohol present and some chloroform; the remainder of the alcohol distils over with part of the chloroform between 59.4° and 61°.[2] For example, the careful fractionation of 500 grams of anaesthetic chloroform made from acetone, containing 0.5 per cent. of alcohol and 0.026 per cent. of water, but otherwise pure, gave the following results:

Temperatures.	Weight of fraction. Grams.
55.5–59.4°	10
59.4–61.0°	177
61.0–61.2°	300
Above 61.2°	13

According to Wade and Finnemore,[3] the possible components of constant boiling point which may be isolated from a mixture of chloroform, alcohol and water are as follows:

Constituent.	Boiling point.	Per cent. chloroform.
Chloroform-alcohol-water	55.5°	92.5
Chloroform-water	56.1°	97.5
Chloroform-alcohol	59.4°	93.0
Chloroform	61.2°	100.0
Alcohol-water (95.5 per cent. alcohol)	78.15°	...
Alcohol	78.3°	...
Water	100.0°	...

Of these seven constituents, the first five may be separated from anaesthetic chloroform containing 0.5 per cent. of alcohol and 0.026 per cent. of water, and the authors have identified the first and third in samples of anaesthetic chloroform containing alcohol varying from 0.5–1.0 per cent.[4] In some cases, it was observed that the first constituent becomes turbid.[5]

It is therefore apparent that the variables of anaesthetic chloroform render the determination of its boiling point of no value as a criterion of purity, since we have here a mixture and no definite compound.

VI. The Decomposition of Chloroform.

I. THE CHANGES WHICH CHLOROFORM UNDERGOES UPON EXPOSURE TO AIR.

There has been considerable diversity of opinion among chemists as to the nature and products of the decomposition of chloroform; in fact, this discordance dates from the introduction of chloroform as an anaesthetic and prevails to-day. This condition is ascribable to the many influencing factors occasioned by the degree of purity of the chloroform under examination, the extent and nature of the exposure; but is principally due to the failure to consider, and therefrom to correctly interpret, the role of the general variable, alcohol, and with it the accompanying moisture.

In 1848, Morson[1] found that "pure" chloroform underwent decomposition in the presence of light and air, chlorine, hydrochloric acid, and probably other "chlorine compounds" being formed;[2] later he observed that the decomposition was variable in extent and rapidity, and that chloroform, when kept under water, did not decompose.[3] Maisch,[4] however, stated that chloroform containing moisture always showed the presence of "free chlorine" much sooner than dry samples.

Hager,[5] investigating the question more extensively, concluded that "pure" chloroform was not decomposed by the action of light alone; but that when chloroform is exposed to the action of the sun's rays, it decomposed, exhibited an acid reaction to test paper, and there were found, among its products of decomposition, hydrochloric acid, "chloroxycarbonic acid."[6] formic acid,[7] and free chlorine. Hager first pointed out that chloroform was decomposed when air had access to it, even in the dark, although then very slowly.[8] Rump[9] made similar observations, having learned that protection from light does not prevent the decomposition of chloroform; he concluded that the smallest quantity of moisture and air would, in time, induce decomposition, and that this, once started, proceeded with increased rapidity. Under these conditions, by excluding the light, Rump found that carbonyl chloride would result.

In 1882, Regnault[10] pointed out that carbonyl chloride was the most dangerous impurity found in

[1] Based on these observations, the authors have devised an extremely sensitive test for the detection of such impurities. This will be given when the tests for impurities are discussed.

[2] Cf. Wade and Finnemore, *Loc. cit.*

[3] *Loc. cit.*

[4] The alcohol was determined by the method of Nicloux (see *Alcohol*).

[5] The presence of water was established by means of calcium carbide (see *Water*).

[1] *Pharm. J.*, **8**, 69.

[2] Therefore, Morson suggested the test with litmus paper and purification by repeated agitation with distilled water.

[3] *Ibid.*, 279. In 1850 (see *Trans. N. Y. Acad. Med.*, **1**, 146), it had been observed in this country that chloroform becomes acid and contains "chlorinated oils" through decomposition.

[4] *Proc. Am. Pharm. Assn.*, **1866**, 264. Chloroform of the density 1.492, dried by means of calcium chloride, was kept in absolutely dry bottles and in bottles slightly moist, then both kinds were exposed to diffused daylight and to direct sunlight. Maisch concluded that the entire absence of water would not be sufficient to preserve the chloroform unaltered.

[5] *Pharm. Z. Russland*, September, 1869.

[6] Personne found that samples of chloroform liable to decomposition always contains "chlorocarbonic ether." It has also been maintained that the change is attributable to the presence of allylene dichloride.

[7] Kappeler (*Anaesthetica*, p. 173) stated that formic acid and aldehyde are products of the decomposition of chloroform.

[8] Hager found that chloroform, even if it does not exhibit an acid reaction, may be in a state of decomposition, and that this condition may be detected by the reaction such chloroform exhibits with ammonia, which then yields with it vapors of ammonium chloride.

The results of Hager's investigation gave rise to the statement which has persisted in the literature till to-day, namely, that specimens of chloroform, originally of good quality, on keeping become impregnated with hydrochloric, hypochlorous, and formic acids.

[9] *Archiv. Pharm.*, October, 1874.

[10] *J. pharm. chim.*, [5] **5**, 504.

chloroform, and stated that it was produced in the presence of light by the action of air on chloroform.[1] In collaboration with Roux, Regnault demonstrated the formation of carbonyl chloride from chloroform in several different ways: By the action of the spark from an induction coil on a mixture of chloroform vapor and air; by allowing air saturated with the vapor of chloroform to circulate in an effluve apparatus;[2] and by the action of ozonized air. The last experiment showed that the production of carbonyl chloride was independent of the thermal and electric phenomena of the other two, and, along with the work of Rump, established the formation of carbonyl chloride during the oxidation of chloroform. Confirmation of this was later had from the investigations of Marty[3] and Stark.[4]

As to just what are the other products of the decomposition of chloroform, is a question which has received considerable, although not very discriminating, attention. Brown[5] found that while chloroform was not decomposed by the action of sunlight in the absence of oxygen, it was so decomposed when oxygen was present, yielding as products *chlorine*, carbonyl chloride, and water:

$$4CHCl_3 + 3O_2 = 4COCl_2 + 2H_2O + 2Cl_2;$$
$$2COCl_2 + 2H_2O = 2CO_2 + 4HCl.$$

These equations have been recognized as correct by Schacht and Biltz,[6] and by Adrian;[7] but Schacht and Biltz considered it necessary to add that they applied exclusively to the decomposition of chloroform which was perfectly free from alcohol. That the decomposition of chloroform is accelerated in an atmosphere of pure oxygen, is a fact which Schacht and Biltz were disposed to ascribe to the absence of nitrogen. At one time they appear to have entertained the idea that ozonization of the oxygen in contact with chloroform and under the influence of sunlight might cause decomposition, but experiments made in reference to this point in 1868, wherein it was shown that no ozonization occurred under such conditions, seem to have induced a contrary view.

In regard to the ultimately recognizable results of the oxidation of chloroform in particular instances—for example, in the case of anaesthetic chloroform—there is one circumstance which exercises a decided determining influence; but, as indicated by Schacht and Biltz,[1] it is not always sufficiently considered, and this fact has given rise to differences of opinion as to the nature of this decomposition and of its products. For instance, Ramsay[2] advanced the opinion that the only products of the decomposition of chloroform are carbonyl chloride and hydrochloric acid, while Brown, Schacht and Biltz, and Adrian maintain that in addition to the formation of those products there is also an elimination of chlorine in the free state. Schacht and Biltz considered that this difference of opinion was doubtless to be ascribed to want of attention to the presence of alcohol in the chloroform experimented with,[3] and to the resulting misinterpretation of the chemical changes which occur. They stated that they had succeeded in proving that the well-known influence of alcohol in preserving chloroform from decomposition[4] was due to the alcohol taking up and chemically combining with the deleterious products resulting from the decomposition, so as to render them innocuous. Later,[5] they concluded that, though the direct products of the decomposition of "pure" chloroform were only chlorine[6] and carbonyl chloride, in the case of chloroform containing alcohol the chlorine thus eliminated acted on the alcohol present, and so gave rise to the production of hydrochloric acid. In this way they accounted for the presence of hydrochloric acid in the first stage of the decomposition of anaesthetic chloroform,[7] and considered that they had explained the point which had given rise to dispute, namely, that the elimination of free chlorine is a primary feature of the alteration. These views led to a controversy with the Browns,[8] and the formation and presence of

[1] Regnault considered the accidental presence of carbonyl chloride common at that time.

[2] Regnault and Roux found that nitrogen charged with the vapor of chloroform also decomposed the chloroform in an effluve apparatus, the products being hydrochloric acid and a mixture of C_2Cl_6 and C_4Cl_6. Cf. the results of Besson and Fournier (*Compt. rend.*, **150,** 1118) on the action of the silent discharge on chloroform in the presence of hydrogen; among the chlorinated derivatives separated were CCl_4, C_2Cl_4, C_2HCl_5, C_2Cl_6, C_3Cl_6, C_3HCl_7, and C_4Cl_8. Cf. Regnault, *Ann.*, **33,** 310; *Ann. chim. phys.*, [2] **71,** 353.

[3] *L'Union Pharm.*, November, 1888. Marty found that "pure" chloroform did not remain unaffected more than two days in summer or 5 days in winter, when freely exposed to air. The same chloroform remained unaltered for 15 months in the dark, although in contact with air. With chloroform containing 0.1 per cent. of absolute alcohol, no decomposition resulted even after an exposure of 15 months to continuous sunlight.

[4] *Pharm. J.*, [3] **20,** 407. Chloroform exposed to diffused sunlight for 5 months contained hydrochloric acid, carbonyl chloride, and an "oily hydrocarbon." According to Stark, the alarming dyspnoea produced by some samples of chloroform when inhaled is probably due to the presence of carbonyl chloride (see *Effects of Impurities*, Section VII, 2).

[5] *Pharm. Soc. Edub.*, March, 1893.

[6] *Pharm. J.*, **1893,** 1005.

[7] *J. pharm. Chim.*, **18,** 5.

[1] *Loc. cit.*

[2] *J. Soc. Chem. Ind.*, **11,** 772. The same view was held by Breteau and Woog, *Compt. rend.*, **143,** 1193.

[3] See *Preservation.*

[4] The correctness of this view, which has been generally favored, will be fully considered under *Preservation.*

[5] *Pharm. J.*, [3] **22,** 1041.

[6] Popov (*J. Russ. Phys.-Chem. Soc.*, **7,** 1061) studied the influence of light on chloroform dissolved in linseed oil, finding that the iodine number of the oil was lowered, owing to the action of the halogen upon the unsaturated compounds of the oil. This work does not, however, prove that chlorine is a product of the photolytic decomposition of chloroform.

[7] Cf. Laurent (*Ann. chim. phys.*, **1837,** 318), who found that chlorine acts on chloroform in the sunlight forming hydrochloric acid and "C_2Cl_8." The opinions of Schacht and Biltz, variously expressed, seem to embody this general view: The gradual disappearance of free chlorine when chloroform is undergoing decomposition is an indication of its further action on the chloroform, producing hydrogen chloride and altering the relative proportions of carbonyl chloride and hydrogen chloride so as to increase the latter.

[8] Schacht and Biltz (*Pharm. J.*, [3] **23,** 1005) stated that "decomposition cannot be detected in alcohol-reduced chloroform until all the added alcohol has been consumed." Brown (*Ibid.*, **24,** 321) found that "pure" chloroform to which 0.077 per cent. of alcohol had been added, when exposed to direct sunlight in colorless glass, began to decompose in 14–19 days. He found that after decomposition had been recognized by zinc iodide and starch, as well as baryta water, reactions were obtained with 1: 2000 potassium dichromate solution and the iodoform test, and these were ascribed to the presence of alcohol. Schacht (*Ber. pharm. Ges.*, October, 1894) defended his position, and stated that the reactions obtained were not produced by alcohol, but by "chloric ether" and "phosgene alcoholide." The Browns (*Pharm. J.*, [3] **25,** 836) maintained that Schacht had not proved that ethyl chloride and chloroformic ether were produced in the decomposition of "alcohol-reduced chloroform," and that they gave reactions similar to alcohol. On the other hand, they considered that they themselves had proved that at the time the decomposition

free chlorine as one of the decomposition products of chloroform containing alcohol were by no means definitely settled.

Schoorl and van den Berg[1] conducted quantitative experiments which seemed to indicate that when chloroform was decomposed by the action of light in the presence of an excess of oxygen, carbon dioxide, water, and chlorine were formed in accordance with the following equation:

$$2CHCl_3 + 5O \longrightarrow 2CO_2 + H_2O + 3Cl_2$$

According to the same chemists, when insufficient oxygen is present—a condition usually obtaining in practice—carbonyl chloride and hydrogen chloride are produced in molecular proportions:

$$CHCl_3 + O = HCl + COCl_2.$$

The equations given by Schoorl and Van den Berg were evidently intended to apply to the decomposition of pure chloroform, and the changes which occur in anaesthetic chloroform were apparently not considered. Schoorl and Van den Berg[2] confirmed the observation that in the absence of air or oxygen, chloroform is not affected by light exposure.

Finally, Dott[3] has suggested that the formation of carbonyl chloride in chloroform very probably occurs in accordance with the following equation:

$$CHCl_3 + H_2O_2 = COCl_2 + HCl + H_2O.$$[4]

Summary of the Present Knowledge of the Decomposition of Chloroform.

From these investigations one may conclude that chloroform free from alcohol, when exposed to air and light, will begin to decompose in a short time; but that this is dependent upon the conditions of exposure—upon the amount of air present and upon the intensity of the light. Consequently the effects produced vary, and chloroform which in one experiment has been found to show decomposition within several hours may, at another time, require an exposure for a whole day, or longer, to full sunlight, before it shows the first indications of decomposition. The temperature prevailing during the period of exposure is also an important consideration. Then again, the nature of the container is of considerable effect in either inducing or retarding decomposition; for instance, in the case of glass, color and solubility should be carefully considered. Details as to these points are usually lacking.

The products of the decomposition of "pure" chloroform, according to various investigators, may be thus summarized:[1]

Chlorine, hydrogen chloride	Morson, Maisch, and Hager.
Carbonyl chloride	Rump, Regnault.
Carbonyl chloride, hydrogen chloride	Stark, Ramsay, Schoorl and Van den Berg, and Dott.
Carbonyl chloride, chlorine	Brown, Schacht and Biltz, and Adrian.

The formation of carbonyl chloride is alone definitely agreed upon.

The decomposition of chloroform has been universally conceded to be an oxidation process. It is generally accepted that chloroform is unaffected by light alone, and that light, although it accelerates oxidation, is not a necessary factor in the process (Hager, Rump, Brown, Schoorl and Van den Berg); however, several investigators appear to have inclined to the view that light is essential, although in noncommittal language, merely stating that it favors decomposition (Regnault, Dott).

If we except the obvious action of water on carbonyl chloride, the influence of moisture on the process of oxidation is still unsettled. In most of the investigations which have been conducted, the presence of water has not been considered; but when taken into account, it has generally been thought to accelerate the decomposition (Maisch, Rump, Dott), although Morson took a contrary view. This consideration is of importance on account of the presence of water in anaesthetic chloroform and, although to much less degree, in the air, and in view of the hydrogen dioxide theory of Dott.

With regard to the changes which occur in anaesthetic chloroform during exposure to air and light, there exists a decided diversity of opinion, principally owing to the fact that no examinations were made during the course of the various investigations, so far as we are aware, for the presence of the oxidation products of alcohol in such chloroform, and the exact role of alcohol in preservation has been consequently misunderstood. Chemists who have studied this phase of the decomposition of chloroform (Schacht and Biltz) have considered that the decomposition is normal, except that hydrochloric acid is formed by the action of chlorine on the alcohol present.

It therefore seemed to the authors that the whole subject required investigation, and accordingly an experimental study of the decomposition of both pure and anaesthetic chloroform was carried out, with particular reference to the following phases of the problem:

1. What are the exact products of the oxidation of pure chloroform?
2. What are the nature and products of the oxidation of anaesthetic chloroform?
3. What part does water play in both cases?

It was thought that the solution of these questions would throw light on, if not fully explain, the role of alcohol and other substances in the so-called pre-

was first recognized by means of zinc iodide and starch, chlorine had not been produced in sufficient quantity to combine with all of the added alcohol, and that ethyl chloride, chloroformic ether or carbonic ether did not give reactions which could be mistaken for those of alcohol.

[1] *Pharm. Weekblad*, **42**, 877. See also the recent experiments of Henrath (*Ann.*, **382**, 222), who found that under the influence of light, and in the presence of water and air, chloroform formed carbonyl chloride and hydrogen chloride.

[2] *Ibid.*, **43**, 8. On exposure to air, in the absence of light, chloroform gave no precipitate with silver nitrate even after four hours, whereas bromoform and iodoform after one hour gave distinct indications of decomposition.

[3] *J. Soc. Chem. Ind.*, **27**, 272.

[4] Support to this view is had from the fact that conditions which favor the formation of hydrogen dioxide a degree of moisture and direct sunlight—are also those which favor the decomposition of chloroform

[1] The reported occurrence of "chlorinated oils" (Gibbs, Stark) and of similar products of the decomposition of impure chloroform is not considered in this summary.

Sample.	No. 1 (Pure).	No. 2 (Pure).	No. 3 (Pure).	No. 4 (Pure).	No. 5 (Pure).	No. 6 (Pure).	No. 7 Anaes	No. 8 Anaes
Description.	35 g. pure chloroform in a 2-oz. bottle of anactinic glass. Exposed 18 days.	A colorless 50 cc. glass, half full of pure chloroform. Exposed 18 days; pungent foreign odor.	10 cc. of pure chloroform in a colorless 100 cc. glass bottle. Exposed 22 days.	100 cc. pure chloroform in a colorless 250 cc. glass bottle. Exposed 22 days.	50 g. pure chloroform in a 5-oz. bottle of anactinic glass. Exposed 23 days.	20 g. pure chloroform and 5 g. water in a 50 cc. colorless bottle. Exposed 18 days.	100 cc. chloroform of density 1.49 over 25 cc. conc. H_2SO_4 for 38 days in a 1-lb. brown glass bottle.	A 100 gr. colorless glass bottle 1/3 full of chloroform containing 0.5% alcohol. Exposed 11 days
$COCl_2$	Trace	Decided reaction	Decided reaction	Marked reaction; sample fumed in air	Faint reaction; slight odor	None	Very pronounced reaction, sample fumed in air	None
HCl	Evidently present	Present	.....	Present	Present	Present in both water and chloroform	Present	None
Grams of acid, calculated as HCl, in 100 cc. of sample.	0.00032	.....	0.004	0.4417	0.0023	Chloroform: 0.0022	0.1440	
Cl	None	Present	.....	Present	See remarks		None	None
Aldehyde	None	None	.....	None	.....	.....	.....	None
Acetic acid	None	.....	.....	.....	.....	.....	.....	Present
Grams of acid, calculated as acetic, in 100 cc.	.....	.....	.....	.....	.....	.....	.....	0.00045 gram increase
Sulphuric acid test	.....	.....	.....	.....	.....	.....	.....	Negative
"Chlorinated decomposition compounds"	.....	.....	.....	.....	.....	.....	.....	None
"Odorous decomposition products"	.....	.....	.....	.....	.....	.....	.....	None
Hydrogen dioxide	None	None	.....	None	.....	Trace in water	None	None
Remarks	Products: Carbonyl chloride, and probably HCl. Cf. No. 2	Products: Carbonyl chloride, HCl and Cl. Cl discriminated from H_2O_2 by mercury and chromic acid test	.....	Absence of H_2O_2 shown by vanadic acid test. Presence of Cl proved	Mercury test indicated Cl or H_2O_2; neither found by other tests. Reaction could be ascribed only to carbonyl chloride	.....	Decomposition due to removal of alcohol present by sulphuric acid. Chloroform became turbid; this was dispelled by agitation with an equal volume of alcohol and acidity became 0.096 gram after 3 hours	Alcohol alone oxidized

Sample.	No. 9 (Anaes.).	No. 10 (Anaes.).	No. 11 (Anaes.).	No. 12 (Anaes.).	No. 13 (Anaes.).	No. 14 (Anaes.).	No. 15 (Anaes.).	No. 16 (Anaes.).
Description.	50 cc. of pure chloroform, containing 1% alcohol, exposed 1 days in a colorless bottle of 120 cc. capacity.	Two samples of chloroform containing 0.74% alcohol and 10% hydrochloric acid exposed for 34 days in colorless glass bottles (1/3 full).	Brown bottle half full of chloroform containing 0.74% alcohol and 0.118% water, exposed 35 days.	65 cc. of pure chloroform with 1.5% of alcohol and 10 cc. of 3.4% H_2O_2 exposed 40 days in 200 cc. brown glass bottle.	50 g. of chloroform containing 0.25% alcohol and saturated with water, exposed for 50 days in a bottle totally filled.	50 g. of chloroform containing 0.25% alcohol under 10 cc. of water for 50 days in a 100 cc. colorless glass bottle.	Anactinic glass bottle full of pure chloroform containing 0.25% alcohol. Exposed 52 days.	A half-pound brown glass bottle of chloroform containing 0.97% alcohol, one-half filled. Examined after 177 and 222 days.
$COCl_2$	None	None in either sample	None	None	.....	None in a free state	None	None in both cases
HCl	None	.....	None	None	None	Present in water layer	None	None
Grams of acid, calculated as HCl, in 100 cc. of sample	.....	.....	.....	.....	.....	.....	.....	.....
Cl	None	None	None	.....	.....	None	None	None
Aldehyde	1:3300	None	1 : 3200	1 : 1660	None	.....	None	After 222 days, 1 : 3500
Acetic acid	Present	.....	Present	Present	Present	.....	Present	Present in both cases
Grams of acid, calculated as acetic, in 100 cc.	0.00022 gram formed during exposure	.....	0.0002 gram formed during exposure	.....	0.00015	0.00135 gram in chloroform layer	0.0006 gram	After 177 days, 0.0003, after 222 days, 0.00135
Sulphuric acid test	Very faint; intensified by formalin	.....	Faint yellow color	Negative	.....	Negative		
"Chlorinated decomposition compounds"	None	.....	None	None	.....	.....	.....	.....
"Odorous decomposition products"	.....	.....	None	None	.....	.....	.....	.....
Hydrogen dioxide	None	None	None	.....	.....	None	None	None
Remarks	Alcohol alone oxidized	Alcohol not consumed	Alcohol alone oxidized	Chloroform apparently not affected	Alcohol alone oxidized	Alcohol originally present consumed; therefore chloroform underwent decomposition. Alcohol added was insufficient under the conditions	Alcohol alone oxidized	Alcohol alone oxidized

Sample.	No. 17 (Anaes.).	No. 18 (Anaes.).	No. 19 (Anaes.).	No. 20 (Anaes.).	No. 21 (Anaes.).	No. 22 (Anaes.).	No. 23 (Anaes.).
Description.	A 2-oz. brown glass bottle 7/8 filled with chloroform containing 0.97% alcohol and saturated with water. 120 days.	A half-pound bottle (unacetinic glass), 5/6 filled with chloroform containing 0.97% alcohol. Exposed 219 days.	A 2-oz. brown glass bottle 7/8 full of chloroform containing 0.97% alcohol. Exposed 220 days.	A 2-oz. brown glass bottle 3/4 full of chloroform containing 0.97% alcohol. Exposed 222 days.	A 2 oz. brown glass bottle 1/5 full of chloroform containing 0.97% alcohol Exposed 222 days.	A 2 oz. anactinic glass bottle 4/5 full of chloroform containing 0.97% alcohol. Exposed 222 days.	An 8 oz. colorless glass bottle 1/4 full of chloroform containing 0.97% alcohol Examined after 120 and 225 days.
$COCl_2$	None	None	None	None	None	None	None
HCl	None	None	None	None	None	None	None after 120 days; faint after 225 days
Grams of acid, calculated as HCl, in 100 cc. of sample	.....	.....	.....	.....			
Cl	None	None. Negative result after 4 mos.	None	None	.....	None	None
Aldehyde	.....	1 : 4000	Trace	Trace	None	None	None detectable
Acetic acid	Present	Present	None	Present	Present	Not determined	Present in both cases
Grams of acid, calculated as acetic, in 100 cc.	0.00025	0.000675	.....	0.00015	0.0009		
Sulphuric acid test	.....	Decided reaction; intensified by formalin	.....	Faint	....	Decided reaction	
"Chlorinated decomposition compounds"	.....	.....	.....	Faint	....	Faint reaction	
"Odorous decomposition products"	.....	.....	.....	None	..	None	.....
Hydrogen dioxide	None	None	None	None	.....	None	None
Remarks	Alcohol oxidized	Alcohol alone oxidized	Incipient oxidation of alcohol	Oxidation products of alcohol alone	Alcohol, but not chloroform, oxidized	Deportment with H_2SO_4 could be attributed only to oxidation products of alcohol	Alcohol completely oxidized

servation of chloroform, an exact explanation of which has been wanting.[1]

Experimental.—Various samples of both pure chloroform[2] and chloroform containing the usual pharmacopoeial amounts of alcohol and water, were exposed, in well-stoppered[3] containers of various sizes, and containing varying amounts of the samples, and of both colorless and anactinic glass, such as are customarily used in the trade, for different periods of time, but at room temperature (20° C.), from September to May, inside of a window having direct southern exposure. The conditions were extreme, but nevertheless were similar to those obtaining in many pharmacies and hospitals.

The anaesthetic chloroform used was examined prior to the experiments, and only such chloroform as was found to be free from all impurities was used. However, an amount of water equivalent, on the average, to 5.1 per cent. by volume of the alcohol was present.[4] Thus each sample was of pharmacopoeial grade.

The method of examination consisted in carefully applying, in duplicate whenever possible, the tests for the detection of the oxidation products of chloroform and alcohol. Whenever possible, the amount of these impurities was determined. The methods used will be detailed in the succeeding portions of this paper, as each impurity is considered.

The conditions and results of each experiment may be seen in the preceding table.

From these experimental results, as well as from others later to be detailed, the authors have arrived at the following conclusions:

1. The products of the oxidation of *pure* chloroform are carbonyl chloride and hydrochloric acid:

$$CHCl_3 + H_2O + O_2 = COCl_2 + HCl + H_2O_2;$$
$$CHCl_3 + H_2O_2 = COCl_2 + HCl + H_2O.$$

We are convinced that oxidation will not occur if water be excluded, and the absolute exclusion of moisture appears to be impossible. Hydrogen dioxide is formed, although we have been unable to detect it in chloroform undergoing oxidation, and therefore conclude that its existence is ephemeral; and oxidation of the chloroform continues throughout the period of the exposure.[5]

The decomposition of pure chloroform is favored by a degree of moisture and is accelerated by light, as is shown by a comparison of the results obtained in the experiments wherein colorless glass was used with those in which anactinic glass containers were employed. Moreover, carbonyl chloride is formed with increased readiness in the presence of acids.[1]

The extent of the oxidation is dependent upon the nature of the container, the amount of air present, the purity of the sample, and the intensity of the light to which it is exposed. In light alone, when no air is present, no detectable decomposition occurs for ordinary periods of exposure; and in cases where there is air contact alone, and no exposure to light, the oxidation is slow.

Free chlorine can only result from the photochemical decomposition of carbonyl chloride:[2]

$$COCl_2 \longrightarrow CO + Cl_2.$$

It is likely that in the cases where "chlorine" was identified as an indication of incipient alteration of chloroform, hydrogen dioxide was the cause of the reactions observed. It will be observed that no chlorine was found by the authors when containers of anactinic glass were used.

This view of the oxidation of pure chloroform is supported in full by the conduct of such chloroform toward ozone[3] and certain oxidizing agents, as, for example, chromic acid,[4] in which case no free chlorine is formed, except possibly through a secondary reaction, and the products are water, carbonyl chloride, and chromyl chloride; and by the analogous case of the photochemical oxidation of iodoform,[5] the primary products of which are carbonyl iodide and hydriodic acid, free iodine resulting only from the decomposition of the carbonyl iodide and from the oxidation of the hydriodic acid. In the case of pure chloroform, the whole reaction is also the sum of a purely photochemical process, since, according to our experiences, free chlorine cannot result through the oxidation of chloroform itself, except from a secondary process, namely, from the decomposition of carbonyl chloride.

2. The products of the oxidation of anaesthetic chloroform are primarily the oxidation products of alcohol, and no decomposition of chloroform itself

[1] See *Preservation*.

[2] This chloroform was prepared according to the method of the authors, already described, and we think that it was absolutely pure.

[3] No cork stoppers unprotected by metal caps were employed. In the experiments on pure chloroform, glass-stoppered bottles were solely used.

[4] The alcohol content of the anaesthetic chloroform used was determined quantitatively by the method of Nicloux (see *Alcohol*).

[5] On the formation of hydrogen dioxide when oxygen is enclosed over water and exposed to light, see Kharichkov, *J. Russ. Phys. Chem. Soc.*, **42**, 904; but see particularly Tian, *Compt. rend.*, **152**, 1072, and Chlopin, *J. Russ. Phys. Chem. Soc.*, **43**, 554.

[1] Cf. Lowry and Magson, *Trans. Chem. Soc.*, **93**, 121, who observed that the formation of carbonyl chloride is evidently accelerated by the presence of acids.

[2] In this connection, see Coehn and Decker, *Ber.*, **43**, 130; and Weigert, *Ann. Physik.*, [4] **24**, 55 (1907). The influence of light on the reversible reaction, $CO + Cl_2 \rightleftarrows COCl_2$, is purely catalytic.

[3] Erdmann (*Ann.*, **362**, 133) has demonstrated that ozone acts on chloroform as follows: $CHCl_3 + O_3 = COCl_2 + HCl + O_2$.

[4] In 1869, Emmerling and Lengyel (*Ber.*, **2**, 546) studied the oxidation of chloroform with sulphuric acid and potassium dichromate. They found but a small amount of carbonyl chloride among the products of oxidation, and incorrectly interpreted the results they obtained, inasmuch as they believed chlorine is formed: $2CHCl_3 = 2COCl_2 + H_2O + Cl_2$. Erdmann (*Ber.*, **26**, 1990) showed that the reaction which occurs is as follows:

$$2CHCl_3 + CrO_3 + O_2 = 2COCl_2 + CrO_2Cl_2 + H_2O.$$

In 1869, Schützenberger showed that carbonyl chloride is obtained in good yield by the action of sulphur trioxide on carbon tetrachloride. On the oxidation of chloroform with chromic acid, see also Cotton, *Bull. soc. chim.*, [2] **43**, 420. On the oxidation of carbon tetrachloride, see Schmidt's "Pharmaceutische Chemie," **2**, 148; and *Ber.*, **14**, 927.

[5] See Plotnikow, *Z. physik. Chem.*, **75**, 337, 385. According to this investigator, the whole reaction is as follows:

$$CHI_3 + O = COI_2 + HI, COI_2 = CO + I_2, 2HI + O = H_2O + I_2.$$

In the light, under constant conditions, the iodine separated is proportional to the time, and if the illumination is removed the reaction still proceeds, but with reduced velocity. There is no separation of iodine in the absence of oxygen, and none in a benzene solution which has not been exposed to light.

occurs while the oxidation of alcohol proceeds.[1] When the oxidation of alcohol reaches a maximum, decomposition of the chloroform goes on as in the case of pure chloroform, with the exception that chlorinated derivatives of the oxidation products of alcohol may result.

The retardation is dependent upon the amount of alcohol present that is, the alcohol acts as a shunt through its capacity for oxidation.[2] The extent of the oxidation is, of course, subject to the conditions referred to under 1. It is important to note, however, that anaesthetic chloroform always contains water, the usual amount being about 0.05 per cent. by volume, according to our experiences.

3. At the inception of this investigation, it was considered possible that the instability of chloroform of all grades might be due to the presence of some catalytic agent, the removal of which would lead to beneficial results, as has been found in the case of sodium hypochlorite,[1] for example. Therefore, this possibility was carefully considered, even though the evidence to the contrary seemed to be of a convincing nature. It was ascertained that the oxidation of alcohol is accelerated by the presence of oxidizable bodies in solution and that foreign organic substances have a detrimental influence upon chloroform—which shows the necessity of having anaesthetic chloroform of a high degree of purity; but we have arrived at the conclusion that, given proper purification, the chloroform prepared from chloral hydrate, alcohol, acetone, or carbon tetrachloride is in all cases identical.[2] In the experiments just cited, only pure chloroform and anaesthetic chloroform were used.

(*To be continued in the May No.*).

LABORATORY AND PLANT

THE ADAPTION OF THE CENTRIFUGAL PUMP TO CHEMICAL PROBLEMS.[3]

By F. G. Wheeler.

Received January 11, 1912.

It has always seemed to me that the machine which is most used in chemical engineering is the one for moving liquids from one place to another, either from one tank to another or to circulate it through various devices for purposes best known to the user. It makes no difference whether the engineer wants to raise water from a mine or to discharge a sludge to a stream, the pump in some form is the most useful agent which can be applied. In all problems of this kind, that kind of a pump which has no valves and which depends alone upon centrifugal force to impart energy to the liquid has appealed to me as the best device which can be selected. As manufactured during the last few years, it moves the liquid with less loss of energy than any other device, stands more abuse and can be operated with cheaper labor than any other machine for this purpose. In the handling of water in quantities above 100 gallons per minute, it is replacing all kinds of steam pumps, except perhaps very large fly wheel engines. It can be used to pump solutions whether they are acid or alkaline, clear or muddy, viscous or mobile. In the use of the centrifugal pump for this chemical service, however, we must have a machine adapted for the heaviest kind of work. It must be built for severe duty from the day it is put into commission to the day it is thrown on the scrap heap.

In selecting a pump for service of this kind, we must consider first whether it will meet the conditions as well as any other device which we could use. I have found that in quantities above 100 gallons per minute the centrifugal will handle any liquid which will flow, or can be made to flow readily. The second point to be considered is first cost. In many instances the first cost of a machine will determine whether it can be applied. Because the centrifugal pump appeared simple, many manufacturers tried to meet all conditions with it, using the cheapest kind of a machine to compete with the steam pump, but it has been shown that it is as expensive to instal a good centrifugal pump at the present time as it is to instal a steam pump, but the former is thoroughly well built and a machine which can compete on the basis of efficiency.

Historically, the pump has been known since the eighteenth century, but the first designs were more like fans than pumps, and were both crude and inefficient. Up to the time when the water turbine was developed the laws which govern the working of a centrifugal pump were but meagrely known, and we have many pumps in operation to-day which were designed before the turbine was developed. When the laws which govern the operation of the reaction turbine were studied, it was learned that the centrifugal pump was in a general way a turbine run backward, and from this were designed various makes of

[1] See *Preservation*.

[2] Additional support to this view is had from the action of pure oxygen on anaesthetic chloroform (q. v.) and supplementary evidence is given under *Preservation*.

[3] Read at the meeting of the American Institute of Chemical Engineers, Washington, December, 1911.

[1] The decomposition of commercial hypochlorite of soda is very largely due to the presence of small quantities of iron as ferrate in the liquor (Muspratt and Smith, *J. Soc. Chem. Ind.*, **1898**, 1096; **1899**, 210).

[2] Trillat (*Nouveaux Remedes*, **1904**, No. 13, 289; *Bull. gen. de Therap.*, **1904**, 46) arrived at a similar conclusion. He undertook to ascertain how chloroform prepared from chloral hydrate compared in point of purity with chloroform prepared from alcohol or acetone, and came to the conclusion that these kinds of chloroform are, after careful purification and rectification, absolutely equivalent. Trillat pointed out that foreign organic substances have an injurious influence upon chloroform, just as do water and air, and he ascribed the change to catalysis. The formation of carbonyl chloride, for instance, he found could be caused by mere contact with the human skin, and this suggested the possibility that it may arise from contact with the mucous membranes This is, however, still an open question, and is hardly supported by the work of Burkhardt (*Munch. med. Wochenschr.*, **1909**, 1678). Such decomposition refers, of course, only to pure chloroform or to such anaesthetic chloroform as contains only a mere trace of alcohol.

We have shown here the necessity of having chloroform of sufficient purity. The care required for its maintenance in an unaltered state will be discussed under *Storage*.

centrifugal pumps which operated much better than the old type. There were many difficulties still to be overcome, and it has been but a few years that we have had a really efficient, commercial machine, which competes with other devices because of real merit.

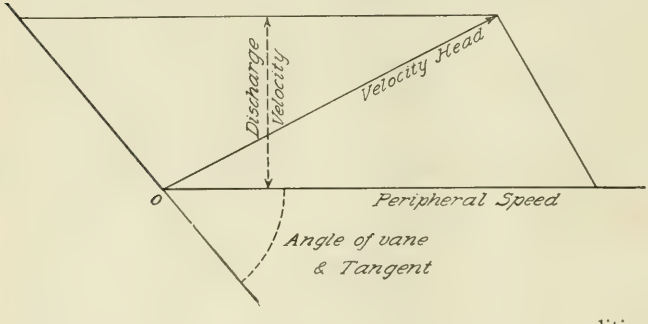
We are all familiar with the cheap centrifugal pump used by contractors and many factories at the present time. I have seen them used in excavations, quarries, paper mills and many other places. They have a two-piece shell, overhung from the support at one side. They are split vertically, and have a single suction on the side opposite from the support. An open fan-like impeller does the work, and enters the casing from the side of the support through a gland which acts like a bearing. It is claimed that this overhung casing has the advantage that the discharge can be turned in any direction. We shall all have to admit that it does have this advantage, which is really that of saving one ell. Its disadvantages are many. There is one modification of this which has a solid scroll and two side pieces, but the principle is the same. The single inlet causes an axial thrust toward the suction, and the first alteration in design was to make the machine with a double suction. This made the casing still further from the support, and to overcome the long overhang, another gland was placed on the outer end of the shaft. This I presume was to be used as a bearing to help support the shaft, but in pumps I have examined, the gland only wore out the outer end of the shaft, either from the vibration of the casing or the strain of the impeller. This overhung casing in some sand pumps was changed to one having a central support. This was considered severe service and it was thought the better method because it decreased the gland wear and helped keep the shaft in alignment. This central support has been almost universally adopted at the present time, but for many years the manufacturers retained the overhung casing as being of advantage in changing the direction of the discharge, and a much cheaper construction. There are still some of these casings used, even with more modern pumps. One maker used the suction pipes to support the casing, but I have seen only those of this one manufacturer supported in this way. All the pumps so far described, are inefficient, inaccessible and crude, because they have a minimum of machine work to make them fit; they are rough castings, thin, and poorly designed. If used for anything but the handling of water they quickly give out, requiring repairs or new castings. The wear on the shaft in the glands, where these were used as a bearing, caused the builders to put in outboard bearings, supported directly from the concrete foundation. Many, however, even at the present time, use the glands as bearings, and the shafts are lubricated in these glands with grease or oil. The next improvement of any importance came about when the laws were studied more closely: the open fan-like impeller was shrouded and finally supplanted by what is known as the enclosed or shrouded impeller. There were many modifications made by different manufacturers, such as the single suction, the double suction, and the double-single suction where the dividing vane came to the periphery. All worked upon the same principle: what entered at the hub must be discharged at the rim. This put more energy into the water, and not so much into friction. Between the sides of the impeller and the wall of the casing, the water revolves only half as fast as it does with the open impeller, because with the open impeller the clearance between the vanes and the sides must be a minimum, and the water must brush the sides as fast as the impeller revolves, where the closed impeller has greater clearance and the speed of the water divides itself between the revolving disc and the sides. This increases the efficiency, and also decreases the wear on the casing. It makes an efficient machine which can be built more easily than an efficient open impeller pump because the clearance need be at only one location. In an efficient open impeller pump, the casing and the sides of the vanes must be accurately machined to fit. With all of the open impeller pumps I have examined, however, the casing and the vanes were only as smooth as the castings fresh from the mold, and no attempt had been made to make the clearance particularly small. I have seen a clearance of over 1/4 inch, and the pump had an efficiency of 20 per cent. I have seen a six-inch pump in a paper mill, lifting about 1000 gallons per minute to a height of about 30 feet (which is about $7^1/_2$ horsepower) being driven by an 8-inch double-ply belt, which was so severely treated that the complaint concerning the pump was that they didn't seem to be able to keep belts on it. The speed of the belt was about 3000 feet per minute, and it should have been able to do 30 horsepower work easily. The only way in which a centrifugal pump with an open impeller can be made to work satisfactorily is to put on a large motor or engine.

The next improvement of noteworthy importance was the splitting of the shell horizontally. Many manufacturers at the present time do not do this, but it lends an advantageous accessibility to the pump. With the shell split in this manner the entire inside of the pump can be opened in a few minutes either to clean out or renew, without disturbing piping or motor. It simplifies greatly the use of renewable running rings which are very convenient with enclosed impeller pumps. Two men can open a horizontally split pump of moderate size, clean it out or renew the rings and have it together again in about one hour. I have seen two men work six hours to open and put together again a pump which has to be taken out endwise. Of course, we are told that the pump is so well made that it doesn't have to be opened very often, but it is not foreseen whether the user will get some chip, or nut or bolt in it; this often happens from new piping or where some repair is being made to an intake. Several of the manufacturers who once made the solid shell pump, are changing to the horizontally split.

There are various difficulties which occur in the

operation of centrifugals, and manufacturers have been working to overcome them. The first trouble of any importance, after the centrifugal was designed according to scientific principles, was end thrust. This was overcome hydraulically by various methods, but there is almost always some unbalanced thrust that will cause trouble if it is not cared for by mechanical means. The thing next in importance is low efficiency. Every effort in both design and construction had been given to create pumps which will deliver the highest possible amount of energy compared to that put in. Large strides have been made, and new ideas are described with great claims for them. There has also been simplification of parts, so that pumps can be built as cheaply as possible. Before taking these up more in detail, I shall recall a few of the principles which govern the design of the centrifugal.

In the first place, I would like to point out that formulas have been worked out for almost every part of every kind of pump. As with the water turbine, the design of the water passages, the shape of the vanes and the peripheral speed of the impeller have to be fixed for a definite amount of liquid against a definite head. If this amount of water is changed in any way whatever, the efficiency will drop; the alteration of the head will also change all of the dimensions. For this reason many manufacturers work out from operating pumps a set of charts which they follow, and the result is that the pump they deliver is not perhaps according to the best theories which have been formulated, but will meet conditions which the other pump will not. Even at the present time, if one wants a very flexible pump in regard to capacity and head, the manufacturers will not guarantee efficiencies very closely. One may work out on the drafting table the exact shape of the water



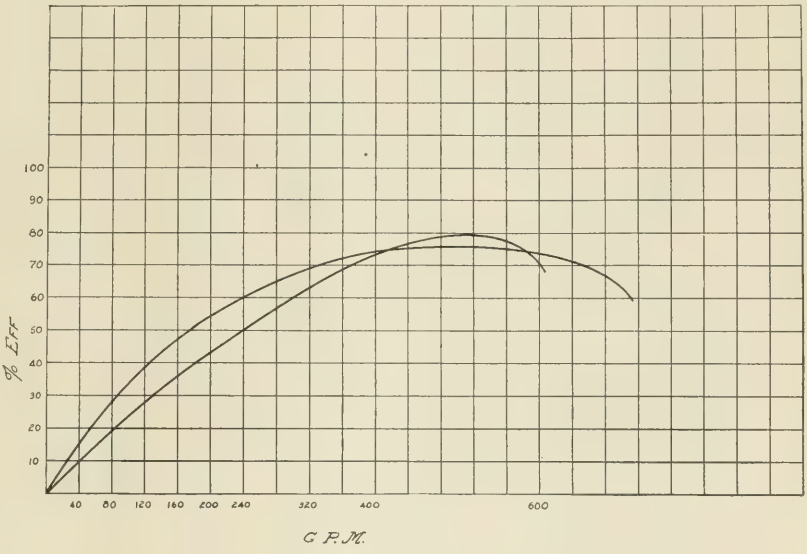
channel, for instance, and any slight error made in the pattern shop, in the foundry or in the machine shop will alter the desired fine point so much that it will be completely lost. After the little alteration is made, and even worked up to the finished pump, a slight change, such as the pressure of the gland on the packing will more than offset the advantage gained. For this reason, we may aim more to accomplish what is wanted in the adaptability of the pump than to gain a small increase in efficiency.

The size of the pump is determined by the amount of liquid and the speed at which it is to be discharged. Usually a speed of 10 to 12 feet per second is used. It is then simple to find the pipe diameter. Secondly, we have to determine the head against which the pump is to discharge. This total head is made up of several different parts—pressure, suction, friction, velocity and orifice heads. If the inlet and outlet of the pump are the same, the orifice and velocity heads are measured as the suction head. The total head then becomes the sum of the pressure, suction and friction heads. To better understand how to adapt a pump to any total head, let us consider what speed must be used to force water up into a very high standpipe. If the water has reached a standstill and nothing is being discharged, the speed of the impeller must be such as to hold the water against that pressure. It can be compared to a falling body, and the velocity of the periphery of the impeller will be the same as that of a falling body, falling from that height in a vacuum. We can easily calculate that speed from the law of falling bodies, $V = \sqrt{2gh}$. For the pressure which the pump can maintain with no discharge this law will be exact, but when the pump delivers water, there are a large number of other factors to be considered. The first factor is the angle between the vane in the impeller and the tangent at the rim. In a general way the larger the angle, the less the pressure will drop with an increased delivery and constant speed and *vice versa*. If the angle mentioned above is small, the pressure will drop; if it is about 30°, it will be almost constant; if 45°, it will rise slightly at first and then drop with increased delivery and if radial or greater than 90°, it will rise almost its entire length. For ordinary work, the different manufacturers have a set of curves which show exactly what each form of impeller will do. These are obtained by testing every pump they make and tabulating the results accordingly. For the working pressure the formula then becomes $V = n\sqrt{2gh}$, where n is dependent upon the angle between the vane and the tangent to the circle. The amount discharged will also depend upon the width of the slot. If we draw a parallelogram with the base equal to the peripheral velocity, the angle between the base and the side that of the tangent of the vane and the tangent of the circle and the altitude equal to the velocity of the water from the impeller, then the diagonal drawn from the angle of discharge will be the velocity head of the water under those conditions. Theoretically the cross-section area of the slot at the rim should be the same as the suction opening at the hub, but many manufacturers make it 85 per cent. of that area, increasing the speed of the water slightly as it passes through the impeller. From this, for a given discharge rate of flow, it is seen that the width of the slot depends upon the diameter of the impeller, which in turn depends upon the speed at the periphery and the working head. Many different kinds of motive powers are used and to meet the speeds of these the pump has to be designed with different impeller diameters so that the proper peripheral speed may be obtained according to the head and vane of the im-

peller. Since the angle of the vane controls the value of n in the formula $V = n\sqrt{2gh}$ many designers keep that angle the same at all diameters, so that the diameter of an impeller can be changed by simply turning it down on a lathe. A spiral having that property is a logarithmic spiral having the equation $\text{Log } \rho = b\theta$ or $\rho = ae^{b\theta}$. It will also be noticed from the law of falling bodies that the head varies as the square of the speed. In other words, if we want to double the head we multiply the speed by 1.414. Also, if we increase the speed at the rim, we increase the speed of the water through the impeller, so that the pump will discharge a much larger quantity of water. The increased amount of water which the pump will throw will depend upon the size of the suction opening and the internal friction of the impeller itself. This can be closely determined by using a constant for the impeller. This constant is equal to the quantity at any given speed, divided by the square root of the head. If then, we determine n in the formula $V = n\sqrt{2gh}$, where n is the ratio between the working head and the shut off head, and then apply the above formula $K = \frac{Q}{\sqrt{h}}$, we can easily determine the quantity which the pump will discharge at the higher speed.

Also, it is shown that at a given peripheral velocity a small impeller run fast is more economical than a large one run slowly, for the smaller impeller has much less surface, and although the friction increases with the speed it increases more rapidly with the larger surface. In the installation of the centrifugal pump, the quantity and the head for which the pump is designed should be adhered to as closely as possible. There will be a narrow range in which the efficiency of the pump will be the highest. Every effort is made to make that range as wide as possible, for under every-day working conditions, we cannot expect the pump which will pump only one quantity against one head to be satisfactory, and the larger the range under which a pump can be used, the better it will be commercially. Some of these difficulties can be overcome by the use of some kinds of motors but they will be considered later.

As stated before, one of the practical problems in the design of a centrifugal pump is taking care of the end thrust. There have been various ways of balancing this hydraulically, but the more important ones are those which were devised by Jaeger and by the Sulzer Bros. in Germany. With single stage pumps, the one devised by Jaeger is used where the pump has an enclosed impeller and but one suction. The idea consists in placing a running ring on the side of the impeller opposite the suction and connecting the chamber so made with the interior of the impeller by suitably placed holes. This and other devices to overcome the end thrust of single suction pumps is very satisfactory as long as the pump does not wear beyond the point of adjustment. In double suction pumps the pressure is hydraulically equal. It is better, however, to place a small collar where it can take up inequalities. There are many little things within a centrifugal pump which might cause thrust, and some of these are utilized by different manufacturers to balance the axial pressures, but the amount of thrust will change with wear and there are usually troubles from this source. Besides the single suction feature, thrusts will be caused by ribs inside the casing. If there is need for repair of a brace inside the casing, the rib or lug will cause an unequal flow on one side of the impeller, and thrust will result. Another cause is that in the casting of an impeller the core is usually made in two pieces, and if these are not placed properly the vane will have a diagonal slant which will cause unequal discharge from the rim. Also there will be an oblique discharge from an impeller, the one side of which is shorter than the other side, or, if an impeller has a piece knocked out of one side, it must be filled in very accurately and carefully, so that there is neither a lug on the side of the impeller, nor an open place in the rim. The best way to remedy this difficulty is to put a ring entirely around the circle, with the piece to fill the opening attached to it. A large number of manufacturers consider it an advantage which increases the efficiency of a pump to use diffusion vanes. If diffusion vanes placed in the casing are not exactly in line with the slot in the impeller, there will be thrust, so that if any are operating a pump having diffusion vanes and, after it has been assembled,



the bearings begin to run hot, it might be from this cause. There is another way of balancing a single suction impeller, and that is by using a disc attached to the shaft and so located that the pressure of the discharge is on one side, and either atmospheric or suction pressure on the opposite side. The criticism of this type is that the wearing joint will increase the leakage, and the thrust will not then be balanced.

To increase the efficiency, I have mentioned the enclosed impeller. The angle of the vane will influence the efficiency for the reason that it will increase or decrease the internal friction by changing the length and cross-section of the channel. Also, the smaller the angle the lower is the working pressure at the same peripheral speed. This necessitates running an impeller with the small angle much faster than one with the larger to obtain the same working head. This creates more friction and a lower efficiency. Since the angle of the vane is determined by the characteristic desired, this loss of efficiency must be balanced against the advantages of the particular characteristic needed. One of the chief losses in the pump with the enclosed impeller, and the only one which will be considered, is the back leakage from the discharge chamber to the suction chamber. This will amount ordinarily to about 5 per cent. Different devices have been used to make this a minimum. Some are simply closely fitting rings, while others are labyrinth packings. The use of a labyrinth, however, necessitates clear water with no grit. Another loss is from eddy currents within the casing. This has led to the use of diffusion vanes. These are vanes shaped in the casing to gradually direct the water from the rim of the impeller to the discharge of the pump. They are used to prevent shock losses. There is a discussion now between the different manufacturers as to the advantage of these vanes, each one claiming the other to be in the wrong. There is only one point which is really interesting, and that is that the one who does not use diffusion vanes competes upon an equal efficiency basis with the one who does. To still lower eddy currents, one manufacturer divides the casing opposite a radial discharge with a vane so arranged that the water must take the shorter route to the discharge opening. This pump seems to show about the same efficiencies as the others. There has been introduced recently a pump in which the diffusion vanes are fixed in a ring that can turn free from the hub of the impeller. The shape of the vanes in this ring are of course different from those in the stationary vane, and it is claimed that this revolving vane increases the efficiency 25 per cent.

There is always the aim to use a more simple design to decrease the price. When a manufacturer has to meet competition, he will frequently offer a pump which is simpler, and for which the same efficiency is guaranteed. It will be seen on close examination that there is a lack of one of the chief features desired—either accessibility, ruggedness of design, or some such point. The pump will have but one bearing, and will depend either upon a gland for a bearing or upon a rigid coupling to the motor shaft, and use the motor bearings. Another scheme is to place the armature of the motor and the impeller of the pump on the same shaft. One manufacturer has brought out a line of both horizontally and vertically split pumps, so that they can be assembled in single or multiple stages to suit the condition. The use of the vertically split shell seems to me to be a poor design for the reason that just where one needs wearing qualities, there is a joint and packing. Also, the distance at the running joint depends somewhat on the packing. With the single piece volute or the horizontally split shell, the running joint is always fixed when the rings are made, and the distance between them is a minimum. I might state here that in replacing a sheet packing at any time in a pump, the new packing should be exactly the same thickness as the original packing, because in machining the case, the work is usually done with the packing in the joint, and in order to have the casing the correct shape, the thickness of the packing must be the same.

When purchasing a pump from the dealers, the details should be most carefully examined. There has always been an impression, created by the first forms of the centrifugal, that this type of pump must be necessarily cheap. For this reason there are many pumps offered to-day which are built entirely on the old lines. These pumps cost about one-third of what a good centrifugal costs, and although the efficiency might be quite high at the start, it soon drops. I have tested new open impeller pumps, which had an efficiency of 18 per cent. These pumps are offered in competition with the better grade, and the efficiency is stated as high or even higher. Some have put enclosed impellers in old casings and so forth. I know of an instance where a firm made inquiry for a pump to handle 5000 gallons per minute against 50 foot head. One of the firms who had been building pumps of the old type had advertised very widely a pump they had just designed and it was thought advisable to give them a chance, more particularly since the size of the pump advertised was the size needed. They had mentioned an efficiency of 70 per cent., and other features known to be of advantage. When the proposal was received, it was the same old design, with the open impeller, the glands for bearings and so forth, which they guaranteed to have an efficiency of 70 per cent. They were asked why they had gone to the trouble of designing and advertising the other pump when the old style was guaranteed at the same efficiency, etc. No answer was ever received. Many of the dealers in the old line advertise the same as the more modern manufacturers and when a purchaser sees that the machine is not up to the guarantee they offer every possible excuse. One of these pumps failed when tried on the work for which it was intended. The pump dealer said that it was the turbine, and the turbine dealer said it was the pump. I have seen them use motors out of all proportion to the efficiency guaranteed. Recently in one of the most modern plants in Detroit, I saw one of these pumps with a 40 horsepower motor

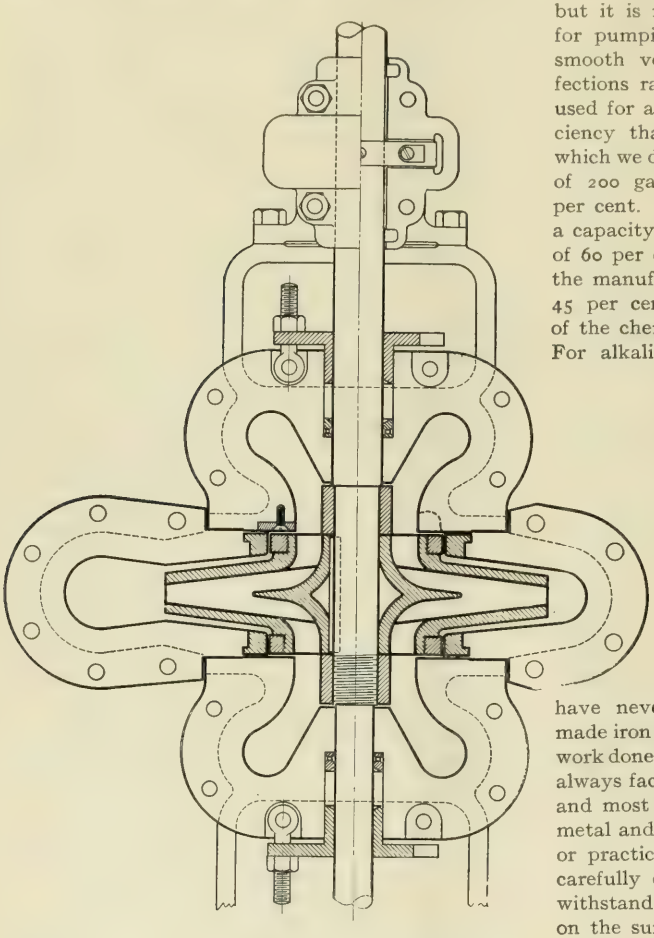
doing 14 horsepower work, and the motor was running so hot that the hands could not be held on the frame. The pump was guaranteed higher than even the most modern pumps can reach, but the motor pulled the load and the outfit was thought satisfactory. The longer an enclosed impeller pump is operated the smoother it becomes and the higher is the efficiency, provided that the running rings are not unduly worn. These can be replaced at very slight cost at any time, and the efficiency will be higher than when the pump was new.

In using one of these pumps for chemical problems, there are many things to consider besides the efficiency, yet this should be kept as high as possible. The pump must meet the conditions, and when the chemical engineer has to pump liquids of different densities from different tanks, at different levels through suction lines of different lengths to tanks similarly situated, the head is by no means constant, the gallonage varies through wide limits, the power required varies sometimes 300 per cent., and the dealer says it cannot be done. Other manufacturers think they can meet the problem, but it is too wide and varied for them to understand, and the pump frequently fails. A pump was purchased by the writer for moving a heavy viscous liquid full of sediment from one tank to another, a firm having agreed to build a special pump at twice the regular price of one made for water. It came and was installed under protest because many parts seemed too light, the slot too narrow, etc. The builder said to instal, and if it did not meet the conditions they would repair. The pump lasted three weeks. The glands were torn out, the sleeves on the shaft were scored and cracked, the liquid had wormed its way into the joint between the impeller and the shaft causing the runner to wobble. It was torn beyond repair, and the running rings were useless. The firm rebuilt the pump, and it is now pumping water. We designed and built our own pump after that trial. In the design of that pump, we eliminated everything we could and built a very heavy design throughout.

In a pump for chemical use where the upkeep is considerable it seems to me that simplicity should be the first consideration. Although small clearances might increase the efficiency slightly, they should be avoided except in the running rings and these should be made easily replaceable. Avoid a labyrinth packing, because it has too close clearances, and will wear excessively. Use single stage pumps, using two rather than one double stage. In this way the use of diffusion vanes are avoided, and narrow passages are not needed except in the impeller. At the exit of the impeller, do not make a narrow running joint, but leave it more like a box. The efficiency may not be as high, but you can then alter the size of the impeller at will, and there are only smooth surfaces within the casing. Secondly, the chemist's pump must be easily accessible. For this reason, we built a horizontally split machine. These are made by several manufacturers, and are very easily opened to clean out a choked impeller, or to renew running rings. Another change which we made on the pump was the separation of the suction opening from the volute. On most of the pumps of this type, unless they are extremely large, the entire volute and suction connections are made in two pieces, but for accessibility and renewals, we separated the casing into seven pieces, the upper half, and the lower half, of the volute, two pieces divided horizontally on each side, and the two suction inlets were joined by a Y pipe. The running rings should be as plain as possible, because all edges will wear. If a passage with an angle in it can be used it will be well to put one in, but each part should be made so that it is replaceable. In all cases I would recommend outboard bearings. These may rise from the base, or be located on cantilever supports from the side of the casing. This arrangement prevents weight and wear coming on the glands, and they can be oiled or adjusted at any time. They should be much heavier than for water and if precipitates are to be handled, I would use heavy thrust collars, for a chunk of material may get into one side of the impeller and none in the corresponding side before the first one is worn down and forced through by the liquid. The result is end thrust which has to be taken up mechanically, and if it is not cared for by a thrust collar where it can be oiled and adjusted, it will either force the shaft over against the motor, or push the impeller over to the side of the casing. I do not think that a marine thrust bearing is necessary, but a thrust collar will not be useless. Frequently, rivet heads, bolts or trash will get into the chemist's pump from open tanks and these will disturb the hydraulic balance of the pump. In pumping precipitates, a screen inserted in the suction pipe increases the suction head on the pump, and sometimes will plug with the precipitate. Before inserting such a screen, the local conditions should be very carefully considered.

The pump for chemical purposes should be built very heavy and rugged. The casing should be made very thick. As a general rule, it seems to me to be much better to build the casing very heavy than to use a thin casing and line it. In pumping alkalis and some acids, the casing can be of the same material as the liner, and the outside skin of the casting will stand more than most materials of which a liner can be made. There is good reason, that of electrolysis, why a lining of a different material should not be used in a chemist's pump. This will be emphasized later. This also applies to sleeves on shafts. It is better it seems to me to replace a shaft, if it is of not too expensive a material, than to use a sleeve. There is always corrosion at the glands, and where there might be electrolysis a sleeve does more harm than good. With the heavy casing should be used heavy flanges. These will stand any pressure which might be put on them from outside. If a pump plugs with a precipitate, the easiest way to clean it out is to put high pressure water on the pump and push the plug out or dissolve it. The heavy casing and flanges will not give trouble under these conditions.

I have seen thin pumps break when this was being done. They will also stand much more water hammer, which sometimes occurs when a pump is pushing the water to the top of a tower or standpipe and is suddenly stopped. I have mentioned the shaft and glands. These should be built heavier than for water and it is better to so shape the casing at the side that it protrudes inwardly to the impeller, because this method keeps the liquid or precipitate from the shaft. No sleeve need be used with this construction, and the casing takes the wear. I have seen these inwardly projecting pieces chew down over one-



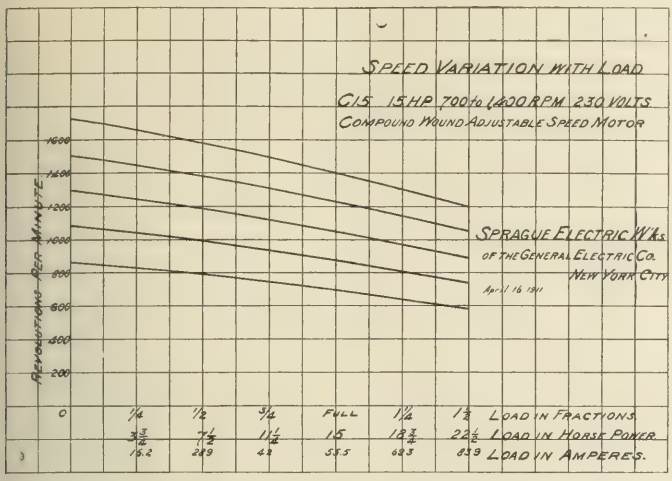
fourth of an inch in eighteen months. We simply machined them back a short distance, and kept them in service. Another point about the gland piece itself is the fact that when there is a liquid pressure on the gland, there might be a slight leakage from the joint where the shaft enters it. It is well to make the gland thick, and put a channel in the outside of the gland piece so that there will be no spray radially from that point. If there is, it will be caught in this channel and from there to suitable receivers. The impeller will wear away faster than any other part. This is due to various causes, and the only way which will really give the best service, is to build it very thick and heavy. For water, the usual thickness is about $^3/_{16}$ inch, but I do not think $^3/_8$ or $^1/_2$ inch too much. I have seen cast iron impellers of that thickness wear out in 4 months so that the thinner impeller would be almost useless. This means special patterns for the manufacturer of water pumps, but it more than pays. In placing the impeller on the shaft, be sure that the liquor will not be able to get at either the key or the shaft. If it does it might cause the impeller to wobble, with results that are obvious. The surfaces should be as smooth as possible, but it is not necessary to make them as smooth as for pumping water. Most solutions will wear them smooth very quickly, and will destroy any imperfections rapidly so that an impeller which has been used for a month will show a very much higher efficiency than the new one. I have seen an impeller which we did not take the time to polish have a capacity of 200 gallons per minute and an efficiency of 25 per cent. Four months later this same impeller had a capacity of 300 gallons per minute and an efficiency of 60 per cent. The efficiency usually guaranteed by the manufacturers of this type of a pump is between 45 per cent. and 58 per cent. In the construction of the chemist's pump various materials can be used. For alkalis an all-iron pump meets the condition very well. When the alkalis are full of a precipitate a harder metal must be used. The running rings may be made of monel metal, or nickel steel.

For some solutions, we can build the pump of bronze, monel metal, hard lead, or stoneware. I do not like stoneware pumps, as the strength of the material is very low, and because of this, slow speed must be used. This means that the efficiency is low, and as I have never seen a stoneware enclosed impeller, the efficiency will be very low indeed. I have never had a stoneware pump tested, but better made iron pumps took power out of all proportion to the work done. One of the problems which the chemist must always face is the speed of the impeller. With water, and most alkalis, the impeller can be made of monel metal and the rim speed can be most anything desired or practical, but in pumping acids, it must be very carefully examined. Many of the metals and alloys withstand acids for the reason that there is formed on the surface a skin of oxide or a salt, which adheres to the metal and protects it. When this is used in a reciprocating pump, the salt is hard enough to withstand the slow speed, but on the rim of an impeller it quickly erodes, and the impeller is dissolved very rapidly. Some alloys which will resist acid for years in tanks, etc., will dissolve in a few hours when made into an impeller. The only way out of the difficulty, is to either use some other form of pump, or to use several pumps in series, keeping the rim speed of the wheels slow enough to leave the protecting skin in place. The multiple stage pump for chemical use has too many complicated parts in one casing.

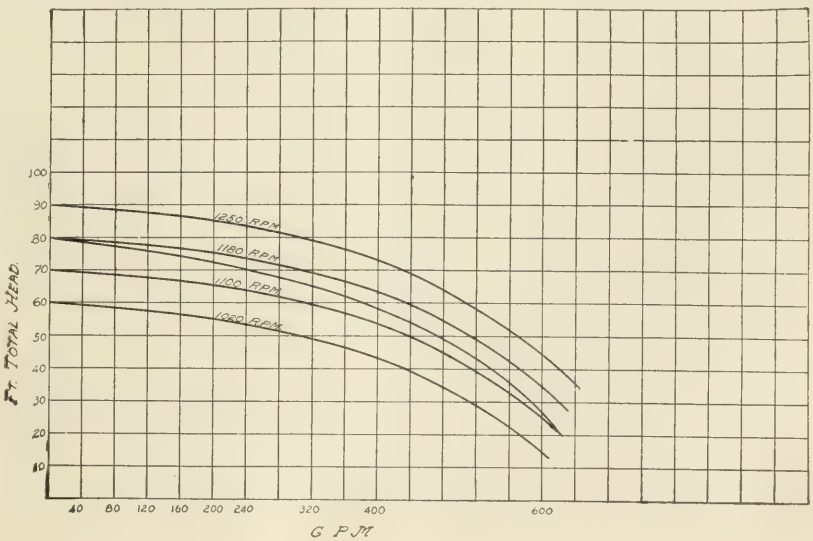
Several single stage pumps in series it seems to me are better, for then trouble can be exactly located and quickly eliminated.

Corrosion also might be from the use of different metals, causing electrolysis. With a rapidly moving surface, which is always clean and bright, electromotive forces will do far more than where sediment is allowed to collect. I have seen monel metal withstand alkali solution for months, even at high speed, and I have seen a monel metal running ring worn out in a month, where a bronze ring was placed next to it. Many times, two metals such as cast iron and mild steel will have an electromotive force between them sufficient to cause trouble, and a peculiar fact is that one may be positive in a dilute solution and the opposite in a more concentrated solution. This is probably due to the fact that the change in the dissociation of impurities changes the real electrolyte. Sometimes it is possible, by placing in the suction line a heavy thick pipe made of a metal which is electro-positive to the material of the pump, to plate and keep plated the inside of the pump, so that both the pump and the pipe will last for a long time, where the pump alone would quickly corrode. This makes the entire outfit practically of one metal, all the different electro-negative parts become polarized, and the corrosion ceases.

When handling precipitates, impellers erode very rapidly. As shown before, the capacity and the efficiency increases, and this will continue until the wheel will drop into three pieces, the hub and the two sides. As it wears, a peculiar cutting action appears on the under side of the impeller vane. This is more pronounced than on the upper side, and it cuts away the outer edges faster than the center leaving a ridge. Not only does the slot become broader, but the outside of the shroud also wears away, about in proportion to the distance from the hub. The wearing is dependent also upon the hardness of the material from which it is made. I have not made scleroscope tests, but government bronze in alkali solutions lasts longer than cast iron, monel will last longer than government bronze, and nickel steel the longest of any tried. These were pumping approximately the same material, containing 60 per cent. by volume of precipitated salts. This property of hardness applies to all parts of the pumps, the running rings even more than the impeller. In using metals for the rings, however, the selection must be made so that there will be no chance of one ring seizing the other. I have had this happen twice with monel metal.



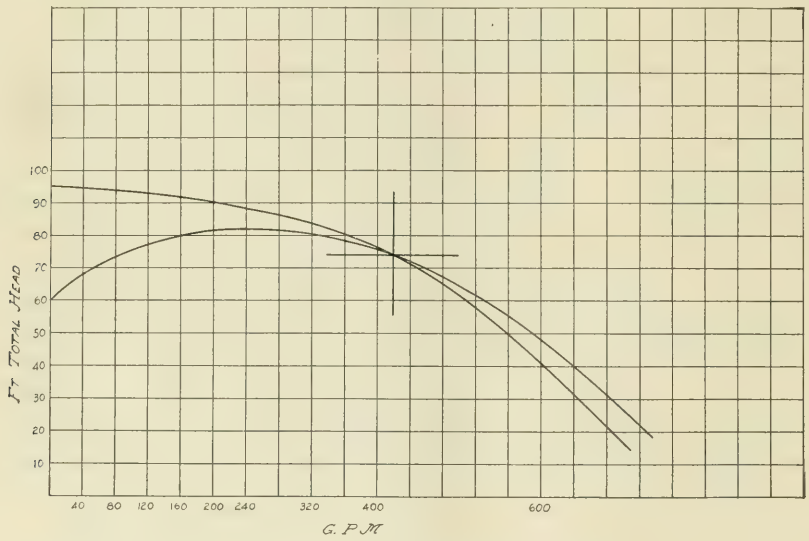
Great care should be taken in providing the stuffing boxes with some means of preventing any possible leakage of air. When handling cold solutions, a convenient means is to place a grease cup in such a way that the packing can be filled with the grease at any time. In this way, the wear on the shaft at the packing is very slight, and no air can break the suction. If hot liquors are being handled, a connection from the volute to a lantern in the stuffing box will effectually prevent trouble, but if there is a precipitate in the liquor it is sometimes necessary to use a clear liquor from some outside source under pressure to keep the gland tight. The most troublesome problem which I have had with these pumps has been in pumping a heavy precipitate with a pressure on the suction of the pump. In spite of a large



stream running into the stuffing box from an outside source, the precipitate will force its way into the packing and cut it into pieces very quickly. I have seen a $^3/_8$-inch packing, 6 rings deep, cut to pieces in one hour, by salt getting into it. In pumping milk of lime, two stuffing boxes had to be repacked twice a day because there was a pressure on the suction of the pump. I inserted a plate in the suction line of the pump, which reduced the pressure to one-inch vacuum, while the pump was running, and the box did not have to be packed for a month. The question of packing has been a difficult one to solve. I have used asbestos, which is usually filled with some cotton. I have also tried asbestos with phosphor bronze wire, and various kinds of metallic packings, but all seem to cut the shafts quickly. The best shafts I have used have been of monel, although I have tried cold rolled steel, government bronze, phosphor bronze and tobin.

There is one point to be made in handling sludges. They are naturally hard to pump. Many of us at first thought would try to overcome this difficulty by using one size larger pipe. In doing this we would make a very gross error. We should use one size smaller pipe, and a pump which will give enough pressure to push the sludge through it. The cause for the precipitate remaining in suspension is the speed of the liquor. If the pipe is large the speed will be slow, and the precipitate will tend to settle out and drag along the bottom of the pipe until it cakes and fills up the pipe to the point where the speed will overcome the settling action of the precipitates. Therefore, it seems to me to use the smaller pipe, using a higher pressure at the pump, and move what was intended is better than to use a lower head pump, and let the pipe fill up which gives a rough surface, and then one has to pump whatever the piping might allow. I have seen horizontal pipes which were carrying hot solutions so hot on top that the hand could not remain on them at all, but comparatively cold on the bottom.

The chemical engineer has to contend with a variable viscosity. This is of far more importance when using a centrifugal pump than in using a reciprocating or rotary device. The mechanical losses in the centrifugal arise from several causes. Among these are mechanical friction, liquid friction, back flow, shock, and eddy currents. When handling water, these each assume some particular percentage of the total loss. A more viscous substance changes both the total and the different component losses. For this reason, pump manufacturers will not guarantee efficiency for anything but water. In both cases the mechanical friction will remain the same for equal loads. There will be a much larger liquid friction due to the fact that the liquid will not flow through the impeller nor allow the impeller to revolve so easily. The back flow will probably be slightly less due to the friction of the slot. The shock and eddy current losses will be more for the reason that the liquid cannot adjust itself so easily to its surroundings. I have been hoping to be able to give you a curve which would show the relative efficiencies of the pump with which I have been working compared to the relative viscosities. Owing to the trouble of measuring the amount pumped and the necessary alterations to accomplish this, I have not been able to work the data out at this time. We may use larger piping and slower speeds if the viscous solutions contain no sediment. The impeller should also be built to deliver at a very much slower speed than for water. In this way, the efficiency might be kept up reasonably high. In using a motor for this purpose, allowance should be made for both the higher specific gravity and the lower efficiency. When calculating pipe friction the viscosity will greatly alter the water rating. When a centrifugal is pumping any liquid, if the head changes, as in changing from one tank to a lower one, it will not affect the working of the pump so much as one might think. Although the pipe may be shorter, and the tank lower, an increased amount of liquor will raise the pipe friction so much that the pump will alter its load but slightly. This may be a more expensive way of pumping than if the pump were made for the lower head but it makes the pump adaptable to both conditions. Frequently a pump can be designed to pump a small amount to a much higher or even a lower head than the normal rating. Each condition must be studied most carefully before installing.



There has been developed a novel pump for the use of chemical engineers which has an application where other machines fail. The most serious difficulty in handling acids is the material of which the pump can be made. A line of hard lead pumps designed like those of 20 years ago, has been on the market for a long time. They cut out very quickly, and most of the trouble is at the gland where the sleeves quickly erode so that the steel shaft is exposed. This pump overcomes all such troubles for the reason that it has no gland, nor packing, and can be made on the most modern lines. The impeller can be either enclosed or open, and it can be built for heads up to even 75 or 80 feet. The shaft is vertical, very heavy and covered with a hard lead sleeve. It is supported from two bearings placed from 3 feet to 6 feet apart according to conditions. The impeller is at the lower end of the shaft, overhung perhaps 6 feet. Around the impeller, is a suitable casing with discharge connections. The suction opening to the casing is the novel feature. It extends upward like an open pipe for about four feet. The liquid to be pumped is simply fed into this open pipe, either at the top, or in the side. The surface of the liquid in this pipe assumes its own form, but as long as there is any in this receiver it will be forced according to the speed and construction of the pump. They can be built of any capacity or head desired.

In closing, I want to mention an arrangement of a centrifugal pump with direct current electric motors. We all know how a series wound motor will operate under varying load. It changes its speed running faster as the load decreases. If in pumping sludges, we use a pump with a drooping characteristic and then use a highly overcompounded motor, the pitch of the characteristic can be made very steep. The operation of a pump under these conditions is such that a decrease in quantity discharged decreases the load on the motor, which instantly speeds up, creating more pressure and removing a plug almost before it has formed. This same idea could be applied to a pump which has a rounded characteristic. As the pressure tends to drop with the quantity on very low discharge, the horsepower will also drop, causing the motor to speed up. The result is that the shut off speed of the motor is higher than the working speed, and the shut off pressure is accordingly higher. If we have to pump into a tower, where the starting pressure must be higher than the operating pressure, this motor will assist in obtaining that result without using the impeller with the longer channels. Many times also, an adjustable speed motor will help us to obtain that flexibility of the steam pump, with the advantages of the centrifugal, with a speed variation of less than 40 per cent.

NEW FORMS OF GAS ANALYSIS APPARATUS.[1]

By G. A. Burrell

Received January 2, 1912.

The gas analysis apparatus here presented were assembled by the author for the conduction of work having to do with the examination of mine and natural gases. The points of novelty involved lie in the entire assemblages. The author took what he considered some of the best features common to some other types of apparatus and assembled them in the apparatus shown.

This particular apparatus is useful for a large class of analyses and quite precise work can be performed with it.

The burette has a capacity of 100 cc. and is graduated in 0.10 cc. Readings can be made to 0.05 cc. The compensating attachment is similar to Hempel's adaptation of Petterson's principle. Mercury is used both in the burette, combustion pipette and manometer tube *j*. The gas sample is drawn into the burette through the 3-way stopcock *g*. The burette is graduated from *g* down. Pipette *a* contains caustic potash solution for absorbing carbon dioxide; *b* contains fuming sulfuric acid for absorbing unsaturated hydrocarbons; *c* contains alkaline pyrogallate solution for absorbing oxygen. These three pipettes contain glass tubes (not shown) for increasing the absorption surface of the solutions as in other Orsat pipettes; *d* and *e* contain cuprous chloride solution for absorbing carbon monoxide. The pipettes *d* and *e* are similar to the pipettes devised by J. E. Babb[1] and used by him for absorbing carbon monoxide from a gas mixture by means of cuprous chloride solution. A side view of the pipette is shown at *m*. The gas mixture as it enters the pipette passes down through the central tube extending into the pipette. It then bubbles up through the solution and lodges in the top of the pipette, forcing the cuprous chloride solution into the reservoir bulb of the pipette. To draw the gas back from the pipette, the stopcock is turned as shown at *m*. Two pipettes of this character when filled with cuprous chloride solution are sufficient, when one of the solutions is kept quite fresh, for the removal of carbon monoxide from mixtures, even when the former is present in great concentration, and for the analyses of any of the industrial gases now used for heating, lighting and power purposes; *f* is the slow-combustion pipette. The slow-combustion method of burning the combustible gases in a mixture, admits of the use of a larger quantity of the residual gas for analysis, than when the explosion method is used. This is especially important when the mixture being analyzed is rich in combustible gases, as natural gas, which contains, not infrequently, 99% of paraffin hydrocarbons. Residual gas left after the absorbable constituents are removed and which is rich in combustible gases is handled in the following manner: The gas is passed into the slow-combustion pipette, and the platinum wire therein heated to a white heat; sufficient oxygen is then introduced into the pipette, at the rate of 10 or 20 cc. per minute, to completely burn the combustible gas. The slow-combustion method possesses a further advantage in that hydrogen or electrolytic gas does not have to be added to a non-explosive mixture for the combustion.

[1] Paper read before the Industrial Division of the American Chemical Society, 45th meeting, Washington, December, 1911. By permission of the Director of the U. S. Bureau of Mines.

[1] Engineers' Society of Western Pennsylvania, **20**, 421 (1904).

For a separate hydrogen determination, the palladium asbestos tube shown attached to *n* is inserted just above the slow-combustion pipette *f*. A small alcohol lamp mounted on a stand provides the necessary heat, about 100° C., for the combustion of the hydrogen.

The pipette *i* contains alkaline pyrogallate solution. Before beginning a series of analyses, air is introduced into this pipette and the oxygen removed. Before beginning a particular analysis, a few cc. of this nitrogen are drawn through the tube *p* into the burette and then discarded into the atmosphere to sweep out of the tube *p* oxygen or other gases left there from a previous analysis. This procedure in conjunction with the drawing of the gas sample into the burette through the 3-way stopcock *g* avoids the so-called capillary error introduced when the gas sample is drawn into the burette through the end of the capillary train, as in the ordinary Orsat apparatus. For less accurate work water can be used both in the burette and slow-combustion pipette.

In Fig. 2 is shown a portable apparatus of the type just described. The gas sample is taken into the burette through the 3-way stopcock *a*. Water is used both in the burette and slow-combustion pipette. Some accuracy is of course sacrificed by the use of water, but the apparatus was built for technical purposes, with the idea of utilizing the slow-combustion pipette for burning methane and hydrogen, and the Babb pipettes for the carbon monoxide determination. Some analysts, however, prefer the explosion pipette. Consequently it can be furnished if desired. The usual capillary error in an apparatus of this type is avoided by using the end pipette for the purposes already described and the drawing of the sample into the burette through the 3-way stopcock *a*. Duplicate determinations should agree within 10 or 15 per cent.

APPARATUS FOR THE ANALYSES OF NATURAL GASES.

The apparatus shown in Fig. 3 is a modification of the apparatus shown in Fig. 1, and is used at the bureau laboratory in analyzing natural gases. Natural gases appear to consist of paraffin hydrocarbons with carbon dioxide and nitrogen present as impurities. Oxygen seems to be present in a sample only as a result of faulty sampling. Carbon monoxide, hydrogen and olefine hydrocarbons have not been found in mixtures thus far examined at the Bureau laboratory. The apparatus shown consists of the pipette *a* for removing carbon dioxide, the pipette *b* for removing oxygen, the slow-combustion pipette *c* and the nitrogen pipette *d*. Mercury is used in the burette and the slow-combustion pipette; 30 to 50 cc. of the residual gas left after the absorbable constituents have been removed can be used for the combustion analysis.

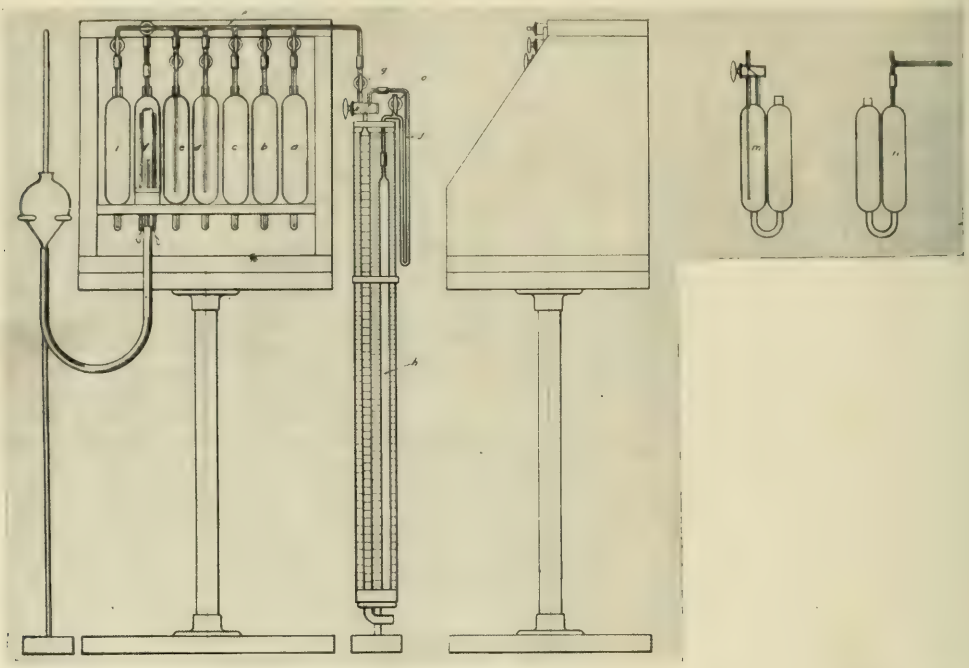


Fig. 1.—Laboratory form of apparatus for mixtures containing CO_2, O_2, C_2H_4, CO, H_2, CH_4, and N_2. Capacity of burette, 100 cc.; burette graduated in 0.1 cc.

MINE AIR APPARATUS.

The apparatus shown in Fig. 4 is a modification of the apparatus designed by J. S. Haldane[1] for the analysis of mine air. The burette has a capacity of 21 cc. and is divided into the ungraduated bulbs at

[1] "The Investigation of Mine Air," by Sir Clement Le Neve Foster and J. S. Haldane, 1905, p. 101.

the top having a capacity of 15 cc. and the stem graduated in 0.01 cc. and having a capacity of 6 cc. The pipette *a* contains caustic potash solution for the removal of carbon dioxide, and the pipette *c* alkaline pyrogallate solution for the removal of oxygen; *b* is the slow-combustion pipette. Mercury is used both in the burette and slow-combustion pipette. Burette readings are made against the pressure of air confined in the compensating tube by bringing the caustic potash solution to the marks *m* and *n*. Carbon dioxide, methane, and oxygen can be determined with an accuracy of 0.02%. Duplicate determinations usually check within 0.01%. Carbon monoxide and hydrogen can be just as accurately calculated from the combustion data by determining the oxygen consumed in the combustion. The apparatus has also been used at the Bureau laboratories for an accurate analysis of the constituents present in flue gases. It can also be used for analytical work connected with other ventilation studies than those having to do with mines.

APPARATUS FOR METHANE DETERMINATION.

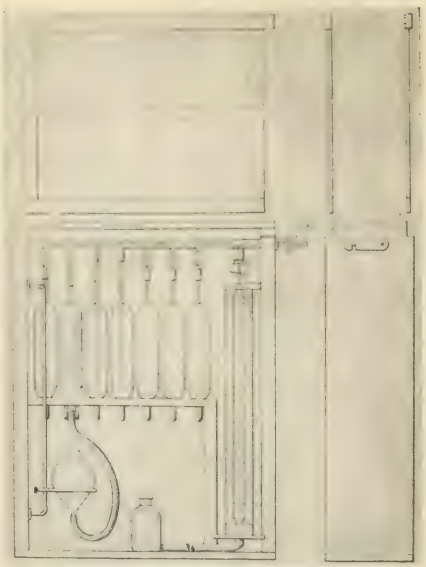
Fig. 5 shows an apparatus constructed for the exact determination of methane in mine air. At a few mines in this country and at many mines abroad, mine air samples are daily collected from different parts of the mine and examined as to their methane content. Winkler's titration method is generally adopted. In Winkler's[1] method the carbon dioxide formed by the combustion is absorbed in a standard solution of baryta water. The excess of baryta water is then determined by titration with a standard solution of oxalic acid. The scheme necessitates a preliminary determination of the carbon dioxide originally present in the mine air.

In the use of the apparatus shown in Fig. 5 the gas sample is drawn into the burette, measured by means of the manometer *b* and compensating tube *c* and then passed into the slow-combustion pipette *g*. The platinum spiral therein is electrically heated and allowed to remain so for three and one-half minutes. After burning, the pipette is allowed to cool and the gas then transferred back to the burette and the contraction in the volume due to the burning of the methane determined. This contraction in volume, when divided by 2 and calculated to a percentage basis, gives the methane originally present in the mine air. Mercury is used both in the burette and combustion pipette. Water is used in the manometer tube *b*. A determination can be made in less than 10 minutes with an accuracy of 0.01%. Methane is the combustible gas commonly found in coal mines, hence complications of the combustion data because of the presence of other combustible gases need not be greatly feared. Paraffin hydrocarbons higher than methane may be occasionally present, but if so usually only in traces.

PORTABLE FORM OF APPARATUS FOR DETERMINATION OF METHANE.

In Fig. 6 is shown portable apparatus similar in

[1] "Hand book of Technical Gas Analyses" by Clemens Winkler, 2nd English edition, translated by George Lunge, 1902, p. 156.



ig. 2.—Portable apparatus for mixtures containing CO_2, O_2, C_2H_4, CO, H_2, CH_4, and N_2. Capacity of burette, 100 cc.; burette graduated in 0.2 cc.; water to be used in the burette and combustion pipette.

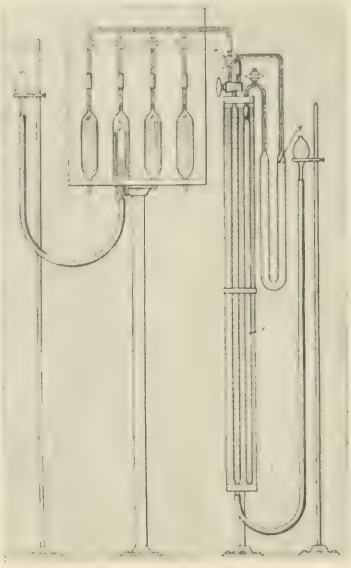


Fig. 3. Laboratory form of apparatus for natural gas analysis. Capacity of burette, 100 cc.; burette graduated in 0.1 cc.

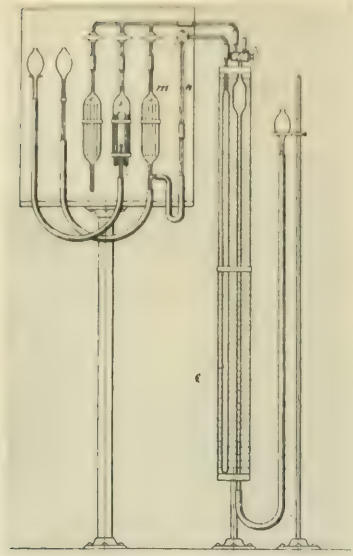


Fig. 4.—Laboratory form of apparatus for the exact analysis of mine air. Capacity of burette, 21 cc.; capacity of bulb of burette, 15 cc.; capacity of stem of burette, 6 cc.; stem graduated in 0.01 cc.

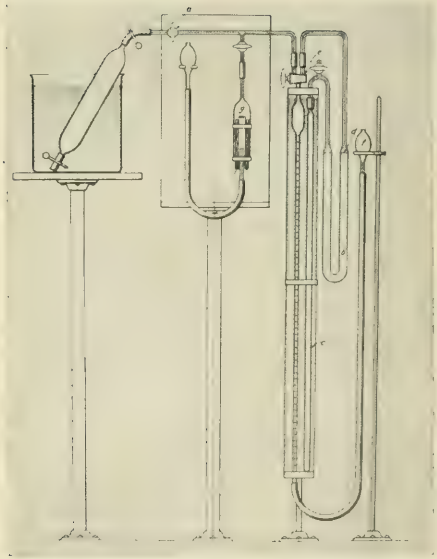


Fig. 5.—Laboratory form of apparatus for the exact determination of methane. Capacity of burette, 21 cc.; capacity of stem of burette, 6 cc.; capacity of bulb of burette, 15 cc.; stem of burette graduated in 0.01 cc.

construction to the one just described. A storage battery can be used to heat the platinum coil. A battery which will produce a current of 6 volts and 4 amperes is required.

In Fig. 7 is shown a portable apparatus which is a very simple form of gas analysis apparatus for the determination of methane. Water is used both in the burette and slow-combustion pipette. *b* is the slow-combustion pipette. It is accurate to 0.10%. This apparatus was devised for the purpose of making a quick determination of methane, for use by mining men who are not chemists. The sample is measured in the burette at atmospheric pressure and then passed into the slow-combustion pipette where the platinum coil is heated to a white heat for $3^1/_2$ minutes. After burning and cooling, the gas is transferred to the burette and the contraction in volume measured. This contraction is divided by 2 to find the methane.

PORTABLE FORM OF APPARATUS FOR THE DETERMINATION OF METHANE AND CARBON DIOXIDE.

In Fig. 8 is shown a portable form of apparatus for the accurate determination of carbon dioxide and methane in mine air. It is a modification of that shown in Fig. 4: *a* contains caustic potash solution, *b* is the slow-combustion pipette. Mercury is used both in the burette and slow combustion pipette.

In Fig. 9 is shown a portable form of apparatus for the accurate determination of carbon dioxide and oxygen in the air of public buildings, meeting-houses, school-houses, etc. It is meant to be used in connection with ventilation studies having to do with those places. *a* contains caustic potash solution and *b* alkaline pyrogallate solution. Mercury is used in the burette.

In Fig. 10 is shown a portable apparatus for the exact determination of carbon dioxide only: *a* is the caustic potash pipette. Mercury is used in the burette. Water is used in the manometer tube.

In Fig. 11 is shown a modified Orsat apparatus used by the author in the analyses of mine fire gases. Considerable aid may be rendered in subduing mine fires by analyzing samples of the atmosphere taken from behind stoppings, in order to determine whether the latter are sufficiently tight to exclude air, or whether, by reason of air in leakage, the embers are liable to fan into a blaze and make conditions worse. Analyses of the atmosphere are valuable to have during the entire period that the fire area is sealed, and before entrances are made to reopen the area.

The apparatus shown in Fig. 11 consists of the burette and the following pipettes: The caustic potash pipette *a*, the alkaline pyrogallate pipette *b*, the cuprous chloride pipette *c* and the slow-combustion pipette *d*. Water is used both in the burette and slow-combustion pipette. The pipettes *a*, *b*, and *c* contain glass tubes (not shown) for the purpose of increasing the absorption surface of the solutions. The apparatus is accurate to about 0.20%.

DETERMINATION OF SMALL AMOUNTS OF CARBON MONOXIDE.

The iodic acid method is used for the determination

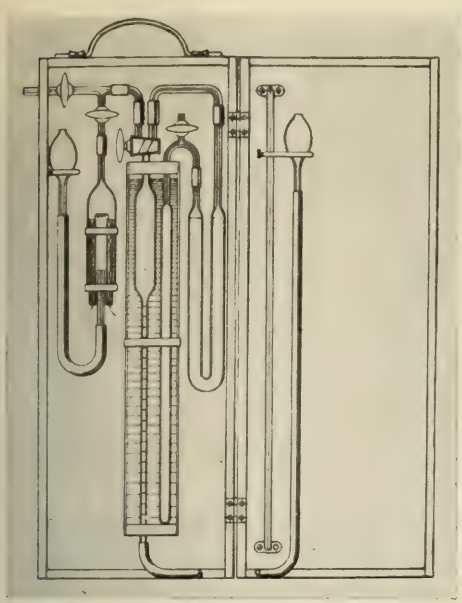


Fig. 6.—Portable gas analysis apparatus for the exact determination of methane. Capacity of burette, 20 cc.; capacity of bulb of burette, 17 cc.; capacity of stem of burette, 3 cc.; stem graduated in 0.01 cc.

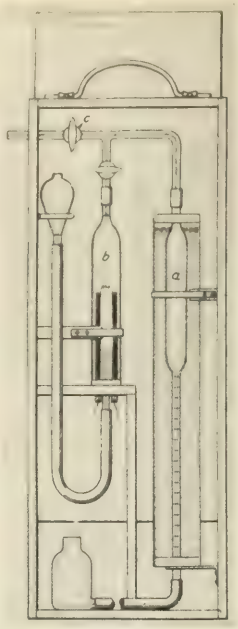


Fig. 7.—Portable apparatus for the determination of methane in mine air. Capacity of burette, 100 cc.; capacity of bulb of burette, 80 cc.; capacity of stem of burette, 20 cc.; stem graduated in 0.05 cc.

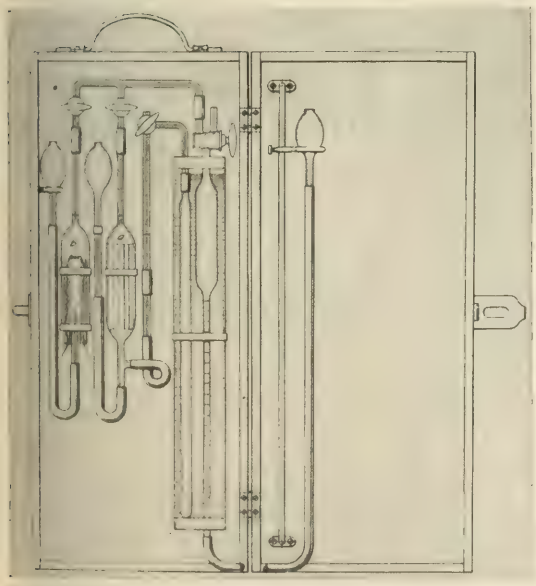


Fig. 8.—Portable gas analysis apparatus for the determination of carbon dioxide and methane. Capacity of burette, 20 cc.; capacity of bulb of burette, 17 cc.; capacity of stem of burette, 3 cc.; stem of burette graduated in 0.01 cc.

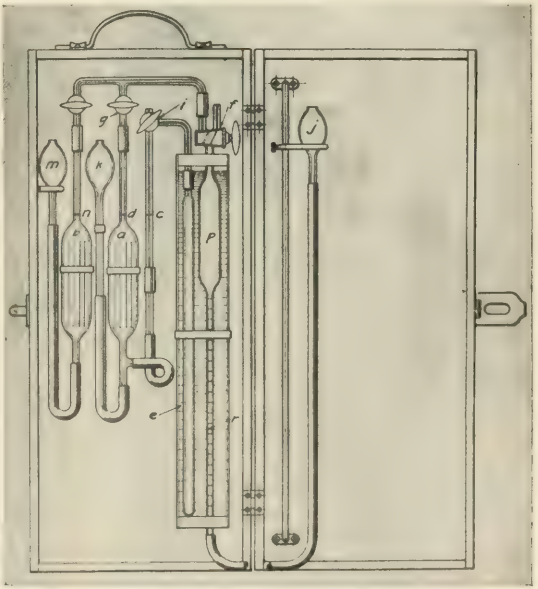


Fig. 9.—Portable apparatus for the determination of carbon dioxide and oxygen. Capacity of burette, 15 cc.; capacity of stem of burette, 3.5 cc.; capacity of bulb of burette, 11.5 cc.; stem graduated in 0.01 cc.

of very small quantities of carbon monoxide. The carbon dioxide formed by the reaction between the

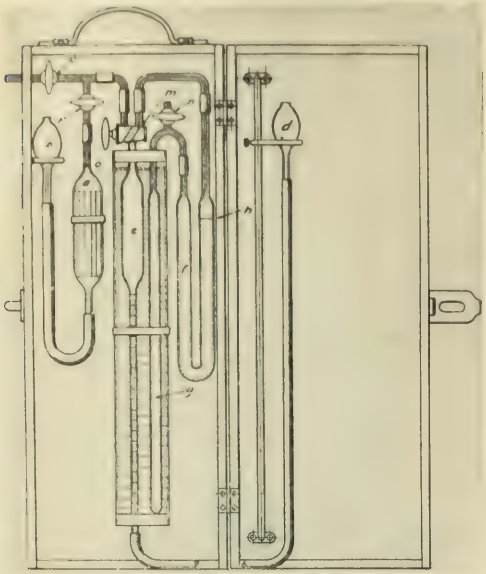


Fig. 10.—Portable apparatus for the determination of carbon dioxide in mine air. Capacity of burette, 20 cc.; capacity of stem of burette, 3 cc.; capacity of bulb of burette, 17 cc.; stem of burette graduated in 0.01 cc.

iodine pentoxide and the carbon monoxide is absorbed by a standard solution of baryta water and the excess of same titrated with standard oxalic acid solution.

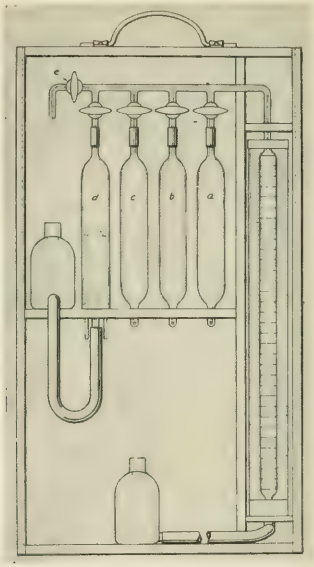


Fig. 11.—Portable apparatus used in fighting mine fires and exploring mines after explosions. Capacity of burette, 100 cc.; burette graduated in 0.1 cc.

The apparatus as used differs from other types in that an electrically wound jacket is used to heat the tube containing the iodine pentoxide and a special burette has been devised for holding the sample.

The burette consists of eight superimposed bulbs, each having a capacity of 100 cc. The constriction between each bulb is calibrated so that any number of bulbs up to eight can be used for holding the sample. The gas is measured in the burette by means of a level bottle, in the ordinary manner: a copper-constantine couple is used for registering the temperature, about 150° C., within the iodine pentoxide tube. These and other devices designed at the Bureau of Mines for examining gases will be fully described in a forthcoming bulletin prepared by the author and his associate, F. M. Seibert.

AN IMPROVED EXTRACTION APPARATUS.

By W. C. Blasdale.

Received December 18, 1911.

Many different forms of extraction apparatus, which make it possible to extract a number of samples with a low-boiling-point solvent simultaneously, have been described. A feature of all the more satisfactory forms of such apparatus is the use of electrical energy in heating the flasks containing the solvent at the desired rate. The apparatus here described utilizes electrical energy obtained from a 110-volt lighting circuit; it provides for five units, that is, for five separate heating plates and condensers. The general form of the rack used to support the extraction tubes and condensers is the same as that described by Hopkins (*J. Am. Chem. Soc.*, **21**, 645). It differs from the latter in that the energy of the current is changed into heat by passing through resistance wire

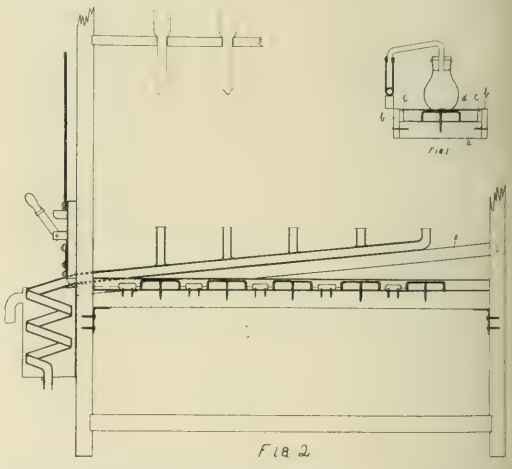


Fig 2

instead of through incandescent lamps, the heat thus generated being imparted directly to the five iron plates upon which the flasks rest. It differs further from any of the forms with which the writer is familiar in that a condenser is attached directly to the frame of the apparatus, which condenser can be easily connected with any or all of the flasks while still in position on the heating plates, thus rendering it possible

to distil off and collect the solvent after extraction has been completed and obviating the need of a separate apparatus for this purpose. The details of construction are represented in the three accompanying draw-figures, which represent transverse, longitudinal and horizontal projections of the lower portion of the apparatus.

The Bed of the Apparatus.—The bed (*a* of Fig. 1) which supports the five separate units consists of a board $5 \times 3/4 \times 24$ inches resting on metal cleats, fastened to the vertical supports as shown in Fig. 2. Two strips of wood (*b* of Fig. 1) $13/4 \times 1/4 \times 24$ inches are nailed to the extreme edges of this support, and two wooden cleats (*c* of Fig. 1) $3/4 \times 1/4 \times 24$ inches are fastened to the base as shown in Fig. 1. The space between the wooden cleats is covered with a strip of one-sixteenth inch asbestos board, and upon this are placed the five heating plates, which are held in position by screws passing into the base. The wooden cleats support a copper plate (*d* of Fig. 1) $5 \times 1/32 \times 24$ inches, which is provided with five

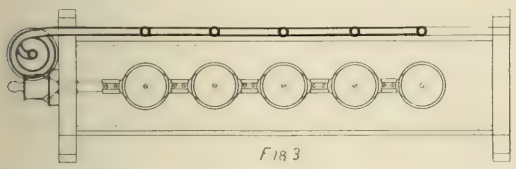


Fig. 3

circular openings of a diameter slightly greater than that of the heating plates. This plate is not fastened in place and can be readily removed for the purpose of inspecting or repairing the heating device.

The Heating Device.—The heating plates were made from the caps used to close the ends of inch and a half water pipes by cutting with a hack-saw to a height of a half inch. These plates are heated by the current carried by a nichrome wire 0.01 inch in diameter which passes from a switch attached to one of the vertical supports through a circuit which includes three complete turns around each of the heating plates. The wire is insulated from the plates by means of strips of mica; it is held in its proper position by means of brass clamps fastened to the bed of the apparatus, each clamp holding two pieces broken from the stem of a Rose crucible, through which the wires are strung. The details of the wiring are best shown in Fig. 3. The total length of wire used was 150 inches and the total resistance offered was calculated to be 72 ohms. An actual measurement of the current consumed gave one and one-half amperes. All the plates were found to be uniformly heated and the heat generated was sufficient to cause ether to boil violently after the switch had been closed for ten minutes. A high boiling-point liquid in one of the flasks attained a temperature of 125°, but no difficulty was experienced in reducing this temperature by interposing a thin piece of asbestos between the heating plate and flask.

The Condensing Apparatus.—A strip of wood (*e* of Fig. 2) $3/4 \times 1/2 \times 26$ inches, nailed to the back of the two vertical supports, sustains the condenser. The latter was made of block-tin tubing a half inch in external diameter and provided with five lateral upright branches, each soldered in place with pure tin. It terminates in a worm condenser, which is enclosed in a cylinder of sheet copper three inches in diameter placed at the end of the vertical support. Connection between the different flasks and the lateral opposite them is easily made by means of a glass tube fitted with cork stoppers as shown in Fig. 1. The entire device takes up but little room and in no way interferes with the use of the apparatus during extraction. Distillation and extraction can be carried on simultaneously on different heating plates provided the laterals of the condenser which are not in use are closed with cork stoppers.

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NOTES ON A NEW FORM OF EXTRACTION THIMBLE.[1]

By P. A. BOECK.

Received January 2, 1912.

The following notes have been collected from the experiences of a number of different investigators, using the new type of inorganic extraction thimbles known as "Alundum."

A few words as to the nature of these thimbles may be of interest: Alundum, the material from which these articles are made, is the product of the fusion of the mineral bauxite (a natural hydrate of aluminum carrying small percentages of iron oxide, silica and titanium oxide) in the electric furnace, in which process partial purification takes place so that the resulting product is essentially pure fused alumina. This material has been used quite extensively for abrasive purposes, replacing emery and corundum, over which it has the advantage of being absolutely uniform and of easily controlled composition. It can be made to yield an abrasive higher in crystalline alumina and consequently of higher abrasive efficiency than any other form of commercial, natural aluminous abrasive.

In the manufacture of laboratory articles of this material, the fused alumina is crushed, graded to uniform mesh, mixed with a small amount of a suitable ceramic bonding material and burned at a high temperature in an ordinary porcelain kiln, where the bond is caused to vitrify or mature, giving it the strength of an ordinary porcelain body, and at the same time retaining its porous nature, which allows the penetration and filtration of liquids and gases.

The porosity of the bodies can be controlled in several ways, which depend, to a certain extent, on the other physical properties, such as strength, thermal conductivity, texture, melting point, expansion due to temperature changes, shrinkage, etc., which are desired. The three methods most generally used in obtaining bodies of different porosities are: (1) by varying the size of the grain or particles of the alundum, thereby changing the size of the voids;

[1] Presented at forty-fifth meeting of the American Chemical Society, at Washington, December, 1911.

(2) by changing the kind; and (3) the amount of bonding materials used. By combining these factors, suitable bodies may be obtained having any texture or porosity for the penetration of liquids of any density. The state of subdivision of the residue which is to be separated from the liquid or gas is of course the final criterion of the permissible size of the voids. In organic extraction work it is particularly desirable to have a porous medium, which gives the most rapid filtration possible with the complete retention of the residue.

Another feature of these thimbles is the fact that no blank extractions have to be made to be sure that the materials are fat-free, as in the case of paper or other organic materials, as, being of a refractory nature, they can be readily cleaned by being ignited at a temperature high enough to dispel any organic material. This also allows of their repeated and indefinite use, so long as no easily fusible inorganic material is ignited in them.

Messrs. Ross and Benner in their work at the Agricultural Experiment Station at the University of Arizona, on the filtration of soil solutions and the separation of "black alkali" in certain characteristic western soils, showed that filters of this material not only filtered more rapidly without changing the concentration of the solution and absorbed less than any other type of filter on the market, but required less washing, were very much more durable and could be cleaned and sterilized by igniting at the proper temperature. For further details, I would refer you to the original paper which is being read in another section of this meeting.

For the extraction and filtration of tanning materials, Mr. R. C. Oberfell describes in the *Journal of the American Leather Chemists' Association* for November, 1911. an ingenious device in which a porous Alundum dish substitutes the asbestos mat, or the mixtures of asbestos and kaolin, for removing the insoluble material in tanning materials. Absolutely clear filtrates were obtained in from $^1/_2$ to 2 minutes without the use of any asbestos or kaolin mixtures in these dishes as against from 82 to 130 minutes using the official method of filtration with the mat, at a consequent saving of about 98 per cent. of the time of filtration, the results of the analyses in each case checking within the allowable error. Where the dish alone was used, no previous saturation or preparation of the filtering medium was necessary, as is the case in the official method.

For organic extraction work on rubber, vulcanized products, fats, waxes, soaps, bitumens. cereals, etc., the proper filtering body for any solvent can be easily made and is apparently limited only by the texture, which must be fine enough to retain the residue and prevent it from penetrating the pores of the thimble. Rapidity of flow and extraction can in this way be increased many times over that obtained with the ordinary extraction thimble.

The chemist of a large rubber reclaiming plant in the west has recently had made an ingenious type of thimble consisting of two thimbles semi-circular in cross-section so made that when fitted together side by side, they occupy no more room than a single thimble, allowing two samples to be extracted at the same time in the same solvent. This method would apply, of course, only in cases where the residues only were desired, the filtrates from the two samples being mixed. The scheme worked out very well at a great saving of time and solvent, and there is no reason why this idea could not be followed out further, and any number of sectional extraction thimbles made to fit one extraction tube.

The application of this type of inorganic extraction thimble has not been limited to liquids, as recent tests indicate that it can be used successfully for the filtration of gases and the separation of dust and fume from air, smoke, producer gas, etc.. quantitatively.

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ADDRESSES

FERTILIZER CHEMISTRY—A REPORT OF PROGRESS.[1]

By PAUL RUDNICK.

Received January 12, 1912.

While it is too early to obtain figures on the consumption of fertilizers in this country for the year just passing, all indications justify the belief that there has been the usual material increase over the tonnage consumed in the previous year, which was estimated, in round numbers, at about 5,750,000 tons, an increase of about 14 per cent. over that of 1909. The average increase in the consumption of commercial fertilizers in the past decade has been something over 11 per cent. annually.

This material increase in the consumption of commercial fertilizers naturally brings up the question of materials entering into this commodity.

[1] Chairman's address delivered before the Division of Fertilizer Chemists, American Chemical Society, December 27, 1911.

The production of organic ammoniates, such as blood, tankage, etc., cannot, under present conditions, keep pace with the greatly increased demand for them. The consumption of nitrate of soda is, of course, keeping pace proportionately with the increased consumption of commercial fertilizers in general. The consumption of cyanamide in this country shows a decided growth, and a plant for its manufacture is now being operated in this country at Niagara Falls. Other products of the utilization of atmospheric nitrogen, such as basic calcium nitrate, do not appear to have gained a foothold in this country as yet. While the annual production of sulfate of ammonia has been greatly increased with the increased installation of retort coke ovens, a great deal more of this valuable ammoniate could be assimilated easily. From the standpoint of conservation of our resources the time should be close at hand when the nitrogen

in practically all the coal consumed will be saved and converted into ammonium sulfate. It is exceedingly interesting to realize that practically all coals contain sufficient sulfur to combine with the nitrogen for production of ammonium sulfate and two different processes are now operated commercially on this plan.

It is a well recognized fact that organic ammoniates must be used in commercial fertilizers in addition to the inorganic ammoniates because of the demand for good mechanical condition, that is, a commercial fertilizer must work in the seed drill or other distributing apparatus without clogging. It is obvious, therefore, that with the increased consumption of commercial fertilizers, there must also be an increased production of organic ammoniates to meet with this requirement. Since the production of organic ammoniates has not been able to keep pace with the increased consumption of commercial fertilizers, very careful thought and study will be required to prevent exclusion of suitable materials by arbitrary methods of analytical control. Unless we can expand our supply of organic ammoniates, the cost of this very necessary class of fertilizer ingredients, which has already increased by leaps and bounds owing to the greatly increased demand, will soon become prohibitive. From a conservation standpoint, it also becomes imperative to utilize any organic nitrogenous material which is now going to waste, if it can be so treated or produced, that it can be shown to have a proper fertilizer value.

There is another point which may well be brought out in this connection, namely that experience has shown that varying availability in the ammoniates of a complete commercial fertilizer is highly desirable, so that there shall be more or less available nitrogen for the plant during the greater period of its growth and not only immediately after the application of the fertilizer.

A great deal of work has been done on the question of making the phosphoric acid in phosphate rock available by cheaper and more efficient means than by acidulation with sulfuric acid. None of the many proposed processes for this purpose, however, has as yet proved sufficiently satisfactory to be operated commercially. Under existing conditions, basic slag is practically confined to the Eastern States. It is to be hoped that a suitable method for producing available phosphoric acid from phosphate rock, other than by acidulation with sulfuric acid, will soon be discovered.

More experimental evidence that phosphate rock itself cannot be used profitably as a fertilizer is accumulating right along. The proposal to use a source of phosphoric acid of little or no availability is in striking contrast to the demand for high availability in the sources of nitrogen, even if the great difference in unit cost is considered.

In this connection the important role of sulfur recently brought out by the Wisconsin Agricultural Experiment Station is of the greatest interest. It is stated that some crops require even more sulfur than phosphoric acid and that the superior results obtained with acid phosphates over other phosphates may not be due entirely to a difference in availability but to the additional sulfur supplied by acid phosphate in the form of calcium sulfate.

Germany continues to be practically the only valuable source of supply of potash salts, and the German potash controversy is so familiar to all that it need only be mentioned in passing. One of the results of this controversy has been to stimulate the search for sources of soluble potash salts in this country to the greatest activity. In spite of repeated denials it appears certain that the source of potash recently announced in Maryland deposits is feldspar and that the proposed method of treatment consists in heating with salt and niter cake. The consensus of opinion, at the present time, is not favorable to the idea that it is possible to utilize feldspar as a profitable source of potash. Fusion or calcination with sodium or calcium compounds causes a material reduction in the percentage of potash, which is already low enough at best in the feldspar itself. The cost of lixiviation and concentration is admittedly prohibitive. The question of utilizing water-insoluble potash is being agitated even in Germany. One of the German Agricultural Experiment Stations reports successful results from the use of finely ground phonolith, apparently a product of the weathering of feldspar, somewhat similar to the zeolites in its nature. Other investigators, however, were unable to obtain such results and insist that this material is worthless as a source of available potash.

The report that the Department of Agriculture had located deposits of soluble potash salts seems to have been premature; it is now understood that sources, not deposits, were meant. It is also announced in this connection that the U. S. Geological Survey has begun actual field operations in the search for deposits of soluble potash salts. A well is being sunk at Fallon, Nevada, and it is to be hoped that the search will prove successful. A coöperative laboratory has been established at Reno, where prospector's samples will be examined. The possibility of finding commercial potash deposits in the arid regions of the west seems to be further indicated by the fact that potassium nitrate is usually present in considerable proportions in alkali soils and indeed the finding of small deposits has been repeatedly reported. The most recent report indicates that such deposits were located in Idaho. So far such deposits have been very small and of very low potash content.

The functions of manganese and boron in the soils are of interest from a fertilizer standpoint. The results so far reported seem to indicate that their function is a catalytic one.

In this connection it is important to note that the A. O. A. C. at its meeting this year adopted as a provisional method a modification of the official method for determining water-soluble potash, consisting in leaching out the water-soluble potash from the sample with hot water much in the same manner that water-soluble phosphoric acid is removed in the determination

of insoluble phosphoric acid. Considerable work has been done on this subject by the Committee on Potash of this Division and the results of the work of this committee indicate that the modified method will give much more nearly the actual proportion of potash put into the fertilizer by the manufacturer. In the official method an average of 0.3 per cent. of water-soluble potash becomes insoluble in the course of extraction.

The theory of the action of fertilizers continues to engage the efforts of many research workers both in this country and abroad as a part of their work on the biochemistry of soils and plants. It has become very evident that the plant food theory is inadequate. Applications of commercial fertilizers which produce large and profitable increases in crops are not nearly sufficient in all cases to replace the elements removed by the plants from the soil. Much attention has been attracted to the discoveries regarding the presence in soils of protozoa which live on and destroy beneficial soil bacteria, of fungi which are harmful either directly to the plants or perhaps to the soil bacteria and of the toxic action of certain constituents of the soil which are either excreted by the plant roots themselves or may be produced by decomposition in the soil. It is easy to believe that fertilizers may exert a beneficial action on the soils to which they are applied by suppressing the activity or harmfulness of such organisms or substances, but it does not follow that this constitutes the entire explanation of the action of fertilizers. The idea that fertilizers may act in part by rendering soluble or otherwise releasing unavailable elements of plant food from the soil is plausible, but lacks confirmation and cannot in any event explain completely the mechanism of the action of fertilizers.

It is more than likely that the theory advanced by Dr. Cameron at our meeting a year ago, namely that no simple explanation can be hoped for, but that the entire matter is enextricably bound up with a large number of other modifying factors such as climatic and meteorological conditions, tilth, drainage, seed selection, etc., is the best we have at present.

It may be well to point out in this connection another possible partial factor in the action of fertilizers. Loeb (*Science*, **34**, 653 (1911)) recently announced that the presence of both potassium and calcium chlorides in sea water is necessary because they exert a protective action on the organisms with which he experimented. These organisms die very quickly in pure distilled water or in a pure sodium chloride solution, as well as in a pure cane sugar solution, and somewhat less quickly when potassium chloride is present in addition to sodium chloride. When both potassium and calcium chlorides are present, however, in addition to sodium chloride, the animals can live for several days. The best proportion of these three salts is that existing in sea water and it is of interest to note that the relative proportion of these salts in human blood is the same as in sea water, although the concentration in blood is much less.

Taking into consideration the fact that practical experience has shown complete fertilizers to be almost uniformly of much more proportional value in producing increased crop yields than incomplete fertilizers, is it not possible that at least a part of the action of complete fertilizers may consist in a similar protective action of their soluble constituents on the cells of the plant? That some action of this sort exists would seem to be further indicated by the results of the extensive researches published on the calcium-magnesium ratio in soils.

With the enormous amount of research work now being carried on in this field, it seems quite likely that we shall soon come to a fairly comprehensive and clear understanding of the more important phases of the mechanism of the action of fertilizers in producing crop increases, so that the most efficient manner of application may be determined with a reasonable degree of accuracy by scientific methods. This is a problem in which producer and consumer alike are interested and its solution will constitute an important chapter in the conservation of our resources.

Efficiency has come to be an important watchword in our every-day life, and much has been accomplished in this direction in agriculture by the use of improved farm machinery. President Taft, in his address on "Conservation of the Soil," before the National Conservation Congress, at Kansas City, last September, quoting from the Yearbook of the Department of Agriculture for 1898, pointed out that between the years 1855 and 1894, the time of human labor required to produce 1 bushel of corn declined on an average from 4 hours and 34 minutes to 41 minutes, and the cost of the human labor required to produce this bushel declined from $35^3/_4$ cents to $10^1/_2$ cents. Between 1830 and 1896 the time of human labor required for the production of a bushel of wheat was reduced from 3 hours to 10 minutes, while the price of the labor required for this purpose declined from $17^3/_4$ cents to $3^1/_3$ cents. Between 1860 and 1894, the time of human labor required for the production of a ton of hay was reduced from $35^1/_2$ hours to 11 hours and 34 minutes, and the cost of labor per ton was reduced from $3.06 to $1.29. In 1899 the calculation made with respect to the reduction in the cost of labor for the production of seven crops of that year over the old-time number of production in the fifties and sixties shows it to have been $681,000,000 for one year. But while it is possible to say that in the future there may be improvements in machinery which will reduce the number of necessary hands on the farm, it is quite certain that in this regard the prospect of economy in labor for the future is not to be compared with that which has been effected in the last 30 years.

To these words of President Taft I wish to add that much profitable progress has also been made in the selection of seeds and in the material and profitable increases of crop yields from the use of commercial fertilizers. While the use of commercial fertilizers commonly shows a material profit, there is doubtless much fertilizer used wastefully because unscientifically. Greater efficiency in this respect can be developed only on the basis of a scientifically accurate theory of the action of fertilizers.

CURRENT INDUSTRIAL NEWS

By W. A. Hamor.

PROGRESS OF THE CHEMISTRY OF PAPERMAKING.

Arthur D. Little presented a full report on this subject at the Thirty-fifth Annual Meeting of the American Paper and Pulp Association, February 15, 1912 (see *Paper* **6**, No. 10, p. 25), from which the following material is taken.

As in a number of other industries—*e. g.*, in glass manufacture—paper-making in the United States is still too frequently regarded as a hereditary art, while in Germany it has become a science. The extent to which the industry has established itself upon a scientific basis is evidenced in the special number of the *Papierfabrikant*, published in June, 1911, and "the publication as a whole cannot fail to impress any thoughtful American paper-maker with the seriousness of the competition which he will ultimately be called upon to meet." Further evidence of the status of paper-making in Germany is had from the 1911 *Proceedings of the Verein der Zellstoff und Papier Chemiker*, wherein abstracts of 305 scientific studies covering almost the whole field of pulp- and paper-making are given, and "at least one other volume will be required to complete the record for the year."

The report of William Raitt, cellulose expert to the India Provinces Exhibition of 1910, published in 1911, contains results of studies on about forty specimens of wood to determine their suitability for pulp-making. These investigations included trial cooks by the standard chemical processes, and Riatt found the sulphate process most generally effective. Riatt concluded that the following species offer the most promising fields for further investigation: *Picea morinda* (spruce); *Abies pindrow* (silver fir); *Bombax malabaricum*; *Trewia nudiflora*; *Salix tetrasperma* (willow); and *Butea frondosa*. His study of the Indian grasses shows that several of these are available in large quantity and furnish excellent sources of paper stock; and he also found that the sulphate process, at any rate with certain species, is adapted for the reduction of bamboo, yielding pulp of such good color that it is immediately available for half-bleached papers. The subject of bamboo as a substitute for wood is to be exhaustively studied at the Indian Forest Research Institute, Dehra Doon. This is of especial interest to Americans in that Richmond has called attention to Philippine bamboo as one of the most promising substitutes for wood for paper-making. Richmond prefers the soda process for its treatment and reports the yield to be 45 per cent.

The straw paper industry, which is highly developed in France, has been described by Abadie. Many different kinds of paper are produced from straw, and in the Limousin paper is made from this material without cooking. Manufacturers in the southwest of France cook the straw in rotary digesters for about four hours with milk of lime.

American paper-makers have been urged to give a more general consideration of esparto, which, according to the experience of English paper-makers, stands in a class by itself as a raw material for the manufacture of high-grade book papers. Great quantities of esparto remain untouched in Algeria for lack of a market. The fiber from the inner bark of the baobab or monkeybread tree is also "deserving of more general utilization." Among other materials, cottonwood is said to yield about 43 per cent. of absolutely dry fiber by the sulphite process.

The most important development of 1911 in connection with paper-making is considered to be the prospect opened out by the new Simmons sugar process of obtaining bagasse or waste sugar cane fiber in great quantities and in a form particularly available as a raw material for paper-making. The large supply of waste fiber obtained under the new process is substantially free from pith, is reduced very easily by the soda process, and yields a pulp suitable for the manufacture of book and printing papers. Cornstalk or maize fiber is said to still have its advocates.

The year marks no notable technical advance in the manufacture of sulphite fiber, but nevertheless considerable attention has been given to the problem of the utilization of waste sulphite liquors. The most important development in this direction is a process introduced in Sweden wherein an impure grade of ethyl alcohol is produced by fermentation of the waste liquor after neutralization with lime. However, this process holds out no hope of avoiding the nuisance created by the waste liquors, since distillery-slop is far more objectionable than the original waste liquor, owing to the presence in it of large quantities of dead yeast. In Germany, attempts are being made to utilize concentrated lyes, after eliminating the sulphurous acid, for cattle feed, but such utilization has not so far been found profitable. The employment of a concentrated liquor for tanning in connection with tannin extracts continues to a certain extent. A method of utilization entitled to careful study is that of Vögel, who recommended that the waste liquor be evaporated, mixed with coal, and then burned. "Saduyn," prepared from the waste lyes of sulphite mills, treated at about 100° C. with sodium chloride, is said to be used in the form of a solution for saturating porous material for the absorption of the vapors of acrolein and other gases in the exhaust of motor cars. Two kg. of the powder is stated to be sufficient for a motor vehicle run of 600 km.

The chemistry of the sulphate process was discussed by Klason and Segerfelt (*Papierfabrikant*, September, 1911). These authors point out that the yields of fiber by the sulphate method are about 50 per cent., while those by the soda process are 37 per cent. With regard to the formation of mercaptan in the sulphate process, it has been proposed that this compound be destroyed by nitrous gases.

At Skutskar, Sweden, the Rinman soda process is in use; soda is recovered by precipitating the organic matter from the waste liquor by means of carbon dioxide in the presence of sodium chloride, and the precipitated material is distilled for the production of acetone and wood alcohol.

It has been proposed that Epsom salt be substituted for alum in rosin sizing. Pauli and also Klemm conclude that, although magnesium sulphate is not to be regarded as a complete substitute for alum, it may replace a considerable proportion of the alum used when used concurrently therewith. Little points out in this connection that in most mills much more alum than is necessary is commonly used.

In coloring, indanthrene blue has been introduced as a substitute for ultramarine. When this dye is employed, it is said to be possible to obtain a back water free from color.

It has been pointed out by Lehman that the waste water loss from paper mills frequently amounts to 10 per cent. of the materials used, and that of this loss fully 90 per cent. is recoverable, even by simple sedimentation methods.

Little urges the establishment of a school of paper-making in this country. It is stated that the matter has been taken up by the Boston Paper Trade Association.

RECENT INVESTIGATIONS ON ALLOYS.

Advance proofs of papers to be presented before the Institute of Metals, issued January, 1912, contain much of interest to the industrial chemist. Abstracts of several of these follow.

Rosenhain, in a discussion on the "Nomenclature of Alloys," directs attention to the confusion which exists at present in the naming of alloys, especially in the use of the terms "brass" and "bronze," which are sometimes employed in contradiction. A system is suggested in which the class name "brass" includes all alloys whose principal constituents are copper and zinc, and "bronze" those containing copper and tin; and when other

metals are present, each particular alloy is distinguished by a prefixed addition to the class name, for example, the so-called "Aich metal" would be termed "iron brass" and "manganese bronze" would be known as "manganese brass."

Bengough, in a paper on the "Properties of Alloys at High Temperatures," gives determinations, through ranges of temperature up to their melting points, of the influence of temperature on the breaking tensile stress and elongation of copper and aluminum, alloys consisting of a single, simple, solid solution (copper-nickel, 70 : 30 brass), and alloys consisting of two solid solutions or other phases (Muntz metal; low-copper brass). In every instance the author finds that the tensile strength diminishes as the temperature rises, although there is generally a change of direction in the curve representing this, most marked in the pure metals (copper, 650° C.; aluminum, 395° C.). Above these temperatures the metals resemble very viscous fluids, possessing little strength, being very ductile, and greatly influenced in their tensile strength by the duration of the application of stress. Stress also causes them to emit a cry like "tin-cry." There are no thermal critical points at these temperatures, and Bengough suggests that in a pure metal the crystals are normally held together by Beilby's "amorphous material," stronger than themselves, in a more or less continuous sheet or cellwork, and that above the "temperature of recuperation" this is no longer capable of existing, and the crystals accordingly come in contact with one another. Fracture now occurs, no longer through the crystals, but along the crystal faces. When a metal is worked at a temperature above the point of recuperation, "amorphous material," if formed, cannot exist permanently, and no effect is produced on the mechanical properties of the metal: this is "hot work." "Cold work," conducted wholly or partially below this temperature, produces "amorphous material" and strengthens the metal. Bengough shows the difference between rolled and cast material in strength by diagrams, and it is seen to vanish at the temperature of recuperation. In the case of pure metals, the elongation may increase, diminish, or remain almost constant, up to the point of recuperation, but there it greatly increases, and remains high until near the melting point.

Turner presents a study of the "Behavior of Certain Alloys when Heated *in vacuo*." He has found that zinc and other metals are entirely removed from brass and other copper-zinc alloys when the latter are heated in a vacuum. With brass, the separation of the zinc is quantitative provided the temperature does not exceed 1200° C. and the heating is not too prolonged. A sample of "poisoned" brass was subjected to this treatment, and it was found that all the zinc, lead and arsenic, and a little of the tin, were removed at 1200° C. Zinc was readily volatilized from 60/40 and 70/30 brass at temperatures of 520° and 550° C., respectively; and when "hard zinc," the residue from galvanizing baths, containing about 5 per cent. of iron, was heated to 500° C., in a vacuum, the zinc was completely volatilized, the iron remaining entirely in the residue. This paper is of great importance on account of the suggested application of the principle to the refining of crude copper, brass scrap, hard zinc, etc.

SILOXIDE

"Siloxide" is a name which has been given to products prepared by fusing pure anhydrous silica with oxides of elements of the silicon-carbon group, as titanium dioxide or zirconium oxide. The new glass is said to be formed by the solution of these refractory oxides of an acid character in silicic acid, and it is stated to be more easily worked than pure quartz glass—in fact, it can be worked by the ordinary methods employed in glass manufacture (see French Patent 432,786, July 31, 1911, of Wolf Burckhardt and Borchers). Z siloxide, or zirconium glass, and T-siloxide, or titanium glass, are now being manufactured at Frankfurt a/M, Germany.

While Z siloxide and T siloxide are said to lack the silky luster of quartz glass ("vitreosil"), yet it is stated [Thomas, *Chem. Ztg.*, **36**, 25 (1912)] that they possess distinct advantages over the latter with respect to strength, resistance to devitrification, and resistance to the action of alkalies.

The best Z-siloxide with respect to strength is said to contain 1 per cent. of zirconia, while that containing 0.5 per cent. has the most satisfactory thermal properties. It is said that zirconium glass has a softening point not much different from that of quartz glass, but that it resists deformation better at high temperatures because of its greater viscosity. The manufacturers state that zirconium glass crucibles are far superior to those made of quartz material in their ability to resist the action of "oxide-bearing metals" during smelting operations; that zirconium glass can be used five or six times; and that it displays only in a very small degree the disagreeable property, inseparable from quartz material, of devitrifying at temperatures exceeding 1300° C. It is supplied in the form of tubes, slabs, concentrating vessels, crucibles, flasks, boxes, muffles, arched-tubes, balls, calottes, etc.

The titanium glasses (0.1 to 2 per cent. of titanium) are said to have a somewhat lower resistance to compression than quartz glass, but to resist transverse fracture better than the latter. The T-siloxide now being marketed is said to be superior to even Z-siloxide with respect to thermal properties—to be more satisfactory when temperatures up to 1500° C. are to be used. Its properties are said to be otherwise the same as those of Z-siloxide. While it is stated by the manufacturers that zirconium glass may be had either transparent or opaque, no information on this point as to titanium glass was secured.

EXTRACTION WITH NAPHTHALENE.

Naphthalene has been known for some time as a solvent for gums and resins (see, for example, English Patent, 14,554, June 30, 1903, to Terrisse), and as a substitute for benzine and benzene, and similar solvents, for spreading purposes in the manufacture of rubber goods (see French Patent, 393,186, August 10, 1908, of the Rütgerswerke-Akt.). Quite recently, a Magdeburg-Sudenburg, Germany, firm has placed on the market a plant for the extraction of bones, plants, fish residues, asphalt, etc., with naphthalene.

As is well-known, naphthalene is volatilized by means of steam; it is this property, in fact, which makes it advantageous as an extractive medium. Temperatures from the melting point, 80° C., to almost the boiling point, nearly 218° C., are said to be applicable; and if this is correct, it is possible to work within wide limits. Further advantages are said to be that the solvent can be recovered from the solutions at relatively low temperatures in comparison with other solvents with similar boiling points; that it is not necessary to employ closed vessels with reflux condensers; and that the use of pressure, generally necessary for dissolving copals, may be dispensed with in the apparatus.

The naphthalene extraction process is said to be particularly applicable for the extraction of bitumen, as "larger quantities of a product of higher melting point are extracted by naphthalene from asphalt-sand or Montan-wax than if one of the ordinarily known extraction substances is used." In one test, 90 per cent. benzene was used, and 19 per cent. of bitumen with a softening point of 70° was obtained; while with the naphthalene process, 23 per cent. of bitumen with a softening point of 81° was obtained from the same material in a shorter period. It is said that for the extraction of asphalt, the low price of the raw material is a consideration. In addition, it is stated that no losses are

incurred and that it is not necessary to resort to such high temperatures that a partial decomposition of the product occurs, in order to effect the separation of the solvent from the asphalt.

The naphthalene process is reported to be of particular value if the bituminous rock, bones, plants, etc., are mixed with about one-half their weight of naphthalene and then extracted by heating. For this purpose, impure naphthalene may be used; it is afterwards recovered as pure naphthalene by treatment with steam.

FIRE EXTINCTION.

The use of frothy mixtures for fire extinction has recently been investigated at Wilhelmsburg, near Hamburg, Germany, in the presence of officials representing the Prussian Fire Brigade (see *Preuss. Feuerwehr-Beirat, Drucksache*, No. 4, 1911; *Engineering*, January 12, 1912, 52. A solution of sodium hydroxide, containing froth-forming ingredients, and a solution containing alum and other chemicals, are mixed together by means of carbon dioxide, which results in the production of a foam consisting of bubbles filled with carbon dioxide; the foam is then directed on to the surface of burning petroleum, tar, etc. It is reported that 2 l. of the mixed liquids, when directed on to light petroleum spirit, gave 13 l. of foam, the volume of which diminished by 5 per cent. in 5 minutes, 14 per cent. in 10 minutes, 47 per cent. in 30 minutes, and 76 per cent. in 1 hour. In one series of tests, the plant employed comprised two reservoirs each of 5 cm. capacity, from which the solutions were delivered to the mixer by two duplex feed pumps at the rate of about 160 l. per minute. The foam was discharged from the mixer through a pipe of 80 mm. diameter, which branched into two pipes of 52 mm. diameter. Fifteen tons of crude petroleum benzine were ignited in a brickwork tank of 10 m. diameter, and after the fire had burned for 5 minutes in a strong wind, the foam was applied under a pressure of 2 atmospheres. The fire was soon stifled except for isolated jets of flame near the edge of the tank, and completely extinguished in 6 minutes; after 10 minutes, on removing the layer of foam, the benzine could be immediately relighted. About 1800 l. of the mixed liquids were consumed. The results seemed to demonstrate that it was advantageous to apply the foam under a low pressure in order that it might spread quietly over the burning surface. Another test was made on burning tar with satisfactory results.

NOTES AND CORRESPONDENCE

THE CENTENARY OF THE INTRODUCTION OF GAS.

The 100th anniversary of the introduction of the use of gas as an illuminant will be celebrated in Philadelphia on Thursday and Friday, April 18th and 19th, 1912. The exercises will be held in the Hall of the Franklin Institute, 15 South 7th Street, and will take the form of a symposium under the auspices of The American Philosophical Society, The Franklin Institute, The American Chemical Society and The American Gas Institute.

PROGRAM.

Thursday: **"By-products in Gas Manufacture,"** by CHAS. E. MUNROE, at 8 P.M.

Friday: **"The Commercial and Financial Aspects of the Gas Industry,"** by GEORGE B. CORTELYOU, at 10 A.M.

"The Technic of Gas Manufacture," by ALFRED E. FORSTALL, at 11 A.M.

"Gas as an Illuminant," by VAN RENSSELAER LANSINGH, at 2 P.M.

"The Use of Gas for Heat and Power; the Testing of Gas," by EDWARD B. ROSA, at 3 P.M.

These lectures will constitute an interesting and valuable review of the development of the use of gas as an illuminant, and as a source of heat and power. Persons interested in the manufacture and use of gas from all parts of the country, members of the societies named, and the general public, including ladies, are cordially invited to attend the sessions.

An effort will be made to bring together as many as possible of the pioneers in the gas industry, those who have been engaged in the industry thirty years or more. All such are requested to send their names to the acting secretary.

A temporary *Loan Exhibition* will be held in the Hall of the Franklin Institute, of articles, models, appliances, books or pictures, that have an historical interest. Any one who knows of such articles should communicate at once with the Acting Secretary, William J. Serrill, 1401 Arch Street, Philadelphia.

AMERICAN ELECTROCHEMICAL SOCIETY, TWENTY-FIRST GENERAL MEETING, BOSTON, APRIL 18th to 20th.

PROGRAM.

The Effect of Addition Substances in Lead Plating Baths. By F. C. MATHERS AND O. R. OVERMAN.

Uniformity and Simplicity in Electrochemical Calculations. By CARL HERING.

Effects of the Variations of Thermal Resistivities with the Temperature. By CARL HERING.

Experiments on Heat Insulation. By F. A. J. FITZGERALD.

An Electrolytic Method for the Reduction of Blue Powder. By WARREN F. BLEECKER.

Tensile Strength of Electrolytic Copper on a Rotating Cathode. By C. W. BENNETT.

The Regeneration of Sulphated Storage Cells. By C. W. BENNETT AND D. S. COLE.

A Rotating Cathode. By C. W. BENNETT.

Electrical Endosmose. By W. D. BANCROFT.

On the Nature of Zinc Cementizing (Sherardizing). By ARDEN R. JOHNSON AND WILLIS R. WOOLRICH.

Smee's Theory of Electrolytic Deposits. By W. D. BANCROFT.

Power Supply to Electric Furnaces for Refining Iron and Steel. By W. SYKES.

Furnace Electrodes Practically Considered. By R. TURNBULL.

On the Volatility of Zinc Oxide. By O. L. KOWALKE.

High Tension Equipment for Electrometallurgical Plants. By J. R. WILSON.

The Influence of Diffusion on the Electromotive Force Produced in Solutions by Centrifugal Action. By W. LASH MILLER.

Vacuum Furnace Metallurgy. By C. G. FINK.

Temperatures of the Carborundum Furnace. By L. E. SAUNDERS.

Gas Circulation in Electrical Reduction Furnaces. By J. W. RICHARDS.

Potential Differences at the Junction of Unmiscible Phases. By R. BEUTNER.

Performance of Dry Cells. By C. HAMBUECHEN.

Report of the Committee on Dry Cell Tests.

AMERICAN COMMISSION ON ORGANIC NOMENCLATURE.

An American Commission on Organic Nomenclature has been appointed, consisting of the following:

M. T. Bogert, Columbia University, Chairman; Ira Remsen, Johns Hopkins University; W. A. Noyes, Univeristy of Illinois; T. B. Johnson, Yale University; M. Gomberg, University of Michigan; J. F. Norris, Simmons College; J. B. Tingle, McMaster

University; C. H. Hudson, Bureau of Chemistry, Washington, D. C.

This commission will coöperate with similar National bodies in other countries in the revision of the Nomenclature of Organic Compounds.

Suggestions as to the general plan to be pursued in undertaking this work, or concerning special groups of compounds, will be welcomed, and should be sent to the Chairman at Columbia University.

EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

Abstract of Announcement No. 3.

This announcement includes the following of special interest and importance:

Ladies' Committee, Committees on Internal Transportation, Entertainment, Finance, Papers and Publications, Trans-Atlantic Transportation, Factory Inspection.

Rules on Papers, their Presentation, Discussion and Publication.—Papers and their abstracts, both in duplicate, must be in the hands of the American Committee not later than June 30, 1912, in order to assure their inclusion, if accepted, in their respective Sectional Volumes for distribution at or before the opening of the Congress.

The Congress obligates itself to have its final Reports and Proceedings, including subject and author index, completed and ready for distribution on or before December 31, 1912.

Rejected manuscripts are to be returned to their authors and all correspondence concerning them is to be regarded as strictly secret and confidential.

How to Obtain Membership in this Congress.—Membership in this Congress is open to individuals, corporations, societies, associations, institutions and the like.

Persons contemplating membership in the Congress can obtain membership tickets from the Treasurer of the Congress, Wm. J. Matheson, 182 Front Street, New York City, by forwarding to him an application for membership and the membership fee, which is $5.00. Membership tickets can also be obtained from Prof. M. O. Forster, 84 Cornwall Gardens, London, S. W., England; M. F. Dupont, 6 Place Malesherbes, Paris, France; Dr. B. Rassow, Stephanstrasse 8, Leipzig, Germany; Prof. Rosario Spalling, Via Panisperna, 89 bis, Rome, Italy.

Membership of Congress Committees does not constitute membership in the Congress.

All memberships received after July 15, 1912, by the American Committee, are accepted on the condition that delivery of printed reports cannot be guaranteed to such members.

Entertainment of Ladies.—The arrangements herefor are in the hands of the Ladies' Committee, and everything will be provided by them to insure the comfort, convenience and entertainment of all ladies attending the Congress. Applications for *Ladies' Tickets*, together with the fee therefor, $3.00, should be sent to William J. Matheson, 182 Front Street, New York City.

Program of Meetings.—The general lectures are to be given by (1) George M. Beiley, of Glasgow, Scotland, "Some Physical Aspects of Molecular Aggregation in Solids;" (2) Gabriel Bertrand, of Paris, France, "The Role of Very Small Amounts of Chemical Substances in Biochemistry;" (3) Carl Duisberg, of Elberfeld, Germany, "The Latest Achievements and Problems of the Chemical Industry;" (4) Giacomo Ciamician, of Bologna, Italy, "Photochemistry of the Future;" (5) Ira Remsen, of Baltimore, Md., U. S. A. (subject to be announced later).

General lectures and general meetings will be held in the Great Hall of the College of the City of New York; Sectional meetings at Columbia University. The Columbia University Gymnasium will be headquarters for Registration, Distribution of Papers, Distribution and Sale of Tickets, Information Bureau, Telephone, Messenger, Telegraph and Cable Services, and Post Office Express and Baggage Facilities.

Columbia University furnishes not only places of meeting and other conveniences as noted above, but also has placed at the disposal of attending members living outside of New York the use of certain of its Residence Halls from August 31, 1912 to 10 A.M., Friday, September 13, 1912. Applications for quarters in these Halls should be addressed to the Eighth International Congress of Applied Chemistry, Residence Hall Committee, 25 Broad Street, New York City.

A list of selected hotels and suggestions for accommodation of parties.

Information concerning excursions and visits to works.

Excursions.—Arrangements in this direction are tentative and very incomplete and the excursions finally selected will depend upon the number of members indicating their desire to join the respective excursions. The itineraries of eight different routes ranging in cost from $11.70 to $435.00 and in duration from 7 days to 44 days are submitted. All of these prices are based upon parties of not less than 100 and do not include hotel charges nor transportation to and from hotels. A map inserted at the end of the pamphlet shows the routes contemplated.

Special Notice.—For the accommodation of those who wish to visit Yellowstone Park, a special tour has been provided for, leaving New York not earlier than August 10th, and not later than August 15th, and requiring about thirteen days with no factory inspection. Members intending to take this tour must notify the Transportation Committee not later than May 15, 1912. Members intending to take part in any of the other trips, must notify the Transportation Committee not later than June 15, 1912. All communications in relation to tours should be directed to "*Transportation Committee*, Eighth International Congress of Applied Chemistry, P. O. Box 1625, Philadelphia, Pa."

Visits to Works.—The list comprises 321 different establishments, located in 144 different cities, and representing 139 different industries or branches thereof. It will, of course, be impossible for the Congress to visit all of these on excursions or set trips. Individual members or small parties of members will be granted permission to visit, by any of the works on the list and not visited by the Congress on excursions or set trips, on presentation of the Treasurer's receipt for membership dues.

Rules governing admission to factories are very strict especially as to visits by *competitors*. Some works will admit competitors but negotiations for such inspection *must be made* by and through Prof. M. C. Whitaker, Chairman, Factory Visits Committee, Columbia Univeristy, New York City.

Special Steamship Accommodations and Rates.—The European participants in the Congress are urged to reserve their accommodations for the westward trip at the earliest possible moment, since the steamships are apt to be very crowded at that season of the year.

CORRECTION.

A CONVENIENT FILTERING APPARATUS.

In the issue of This Journal for March, 1912, page 222, under the article whose title is given above, the name of the author was given as C. S. Williams, Jr., instead of C. S. Williamson, Jr.

THE BUSINESS ASPECT OF THE KELP PROPOSITION.

By Frederic P. Dewey.

Received February 17, 1912.

It is thoroughly well established that the giant kelps of the Pacific provide an enormous store of KCl. Various papers have appeared upon the broad, general aspect of the question, but for the most part they have dealt in glittering generalities and many of them have started in the middle of the proposition. Many writers neglect or slur over the gathering and preliminary drying of the kelp, and base their real consideration of the subject upon the air-dried material. This is very attractive and easy to do, but the cost of the air-dried kelp is a most serious business consideration.

There are various technical and business problems connected with the matter. Without in the least doubting the eventual solution of these problems, it may be said with entire safety that their solution with financial profit will require the expenditure of much time and money, under the best technical and business direction, and that it must be several years before KCl from kelp can become a commercial commodity, if it ever does.

The consideration of the subject divides itself naturally under the following heads:

Harvesting the kelp.
Air-drying.
Oven-drying.
Distillation.
Crystallizing KCl.
Marketing.

To start with the growing kelp. How can it be harvested? It will be an entirely new industry and manifestly various machines of different types will have to be constructed and subjected to actual practical tests before an efficient and economical machine is secured. Dr. Cameron[1] has suggested 1,000,000 tons of KCl as a conservative annual yield. This would mean the harvesting of approximately 30,000,000 tons of kelp. This harvesting cannot extend over the whole year. Just how long it may last cannot yet be definitely known, but in any event the vast machinery required to harvest 30,000,000 tons in a short season must stand idle a good part of the year at a heavy interest charge against the product.

Having brought the kelp to shore it must be dried. To produce a ton of KCl, approximately 27 tons of water must be evaporated. Clearly the most inexpensive natural means for drying must be adopted, but even this would require the construction of drying sheds covering an enormous area and the building of especially designed machinery to distribute the wet kelp on the drying shelves and to gather up the dried stuff. As with the harvesting machinery, these sheds and machinery must remain unemployed a good part of the year.

There is, however, a limit to the extent that natural drying in open sheds can be carried. When about 25 tons of our 27 tons of water have been evaporated, provision must be made to protect the efflorescing KCl which will soon be produced on further drying. This will require the application of artificial heat. It may possibly be assumed that this can be obtained from the kelp itself in a subsequent operation. By proper oven-drying it is possible to recover 40–50 per cent. of the KCl as effloresced salt by simply shaking it off from the dried kelp.

The recovery of the balance of the KCl from the dried and shaken kelp requires the breaking up of the organic matter of the kelp body and this must be done with as full as possible utilization of its value. Simple burning with the utilization of its heat value only will not be sufficient, even if we now had a furnace adapted to avoid enclosing unburned material in the inorganic salts by sintering and to avoid undue loss of KCl by volatilization.

[1] This Journal, 4, 77.

At present, there does not seem to be any method available for this part of the work except destructive distillation with the recovery of the condensable by-products and the utilization of the gas, first to heat the retorts, and secondly, for the oven-drying of the kelp as far as may be. Probably there are no technical difficulties in this operation, but it must be remembered that only about half of the weight, including the effloresced KCl, of the oven-dried kelp is organic matter. In other words, broadly speaking, in the production of one ton of KCl only one ton of organic matter is available for the production of by-products of distillation. On the other hand, the total production of such by-products in the recovery of 1,000,000 tons of KCl would be so large that much of them would have to be transported long distances to find a market and therefore the profit of the operation would largely depend upon freight conditions.

Undoubtedly a limited amount of the residue from the retorts could find direct application as a fertilizer within a certain radius, but the real market for KCl is on the Atlantic coast, and under the present freight conditions of 80 cents per 100 lbs. the KCl must be dissolved and recrystallized. Upon the opening of the Panama Canal and the expected halving of the freight rates, the distillation residue might possibly better be shipped direct.

The mother liquors from the recrystallizing of the KCl will contain iodine and when sufficiently enriched they may be treated for the recovery of this element.

It would be a liberal estimate to assume that the by-products recovered including the iodine, would have a value sufficient to pay for all of the operations upon the air-dried kelp. If we do this and also assume that after sufficient trial and development of the necessary machinery the kelp can be harvested for 25 cents per ton and air-dried for 15 cents per ton more, a ton of KCl laid down on the Atlantic coast would cost $28 as follows:

Harvesting 30 tons at 25 cents	$7.50
Air-drying 30 tons at 15 cents	4.50
Freight 1 ton at 80 cents per 100 lbs.	16.00
	$28.00

On the completion of the Panama Canal it is expected that the freight will come down to $8 per ton, but the present prices of KCl must be very profitable to the German Potash Syndicate and if actually faced with the possible loss of its American trade the prices would undoubtedly be reduced. This reduction might even wipe out the advantage of the low water-freight.

In conclusion it would appear that the feldspars have not yet been displaced by the kelps as a possible source of potash.

Washington, D. C.,
February 16, 1912.

IMPORTATIONS OF ACETIC ANHYDRIDE.

The importation of acetic anhydride, which for some years has been steadily on the increase, is showing since last March a very rapid decline, according to the figures published by the quarterly report of the Department of Commerce and Labor on Imported Merchandise Entered for Consumption in the United States. The amounts in pounds imported during the quarters ending at dates given and their valuations are as follows:

Sept. 30, 1910, 202,227 lbs., $38,531; Dec. 31, 1910, 266,204 lbs., $50,838; March 31, 1911, 504,536 lbs., $93,501; June 30, 1911, 197,518 lbs., $35,806; Sept. 30, 1911, 117,093 lbs., $20,842.

This sharp decline in the consumption of acetic anhydride is probably due to the abandonment of the manufacture of cellulose acetate films for photographic purposes.

CONSULAR AND TRADE NOTES

ENGLISH MUNICIPAL GAS WORKS.

Consul Edward B. Walker, Burslem, advises that the report for the year ended March 31, 1911, of the gas department of Stafford, population 25,000, contains some interesting information and figures. The gas works have been in the possession of the municipal corporation for 33 years, during which time the bonded indebtedness has been reduced from $550,673 to $182,189, a reserve fund has been provided, and municipal taxes have been reduced $286,019. The price of lighting gas is $0.65 per 1,000 feet, with discounts up to 10 per cent. according to consumption, and $0.48 per 1,000 feet for power, with discounts up to 25 per cent., reducing the price all around to about $0.37.

The gross receipts during the year in question were $162,899 and the expenditures $93,930, leaving a gross profit of $68,969. Loans repaid, interest, etc., amounted to $31,447, and the net balance was distributed as follows: District fund in reduction of taxes, $17,033; free library, $243; suspense account, $6,083; reserve fund, $9,755; carried forward, $4,408. The town had a profit-sharing scheme under which the workmen received a bonus of over 10 per cent. of their wages. The amount of gas sent out was 211,852,000 feet, of which 4,358,630 feet was unaccounted for, or leakage. The coal used was Staffordshire "washed beans," costing about $2.68 per ton.

The gas business is managed and treated as a separate undertaking. All salaries of officials and expenses of management and operation are included in the balance sheet, and the corporation pays taxes as would an ordinary company.

UTILIZATION OF NATURAL GAS IN HUNGARY.

Consul-General Paul Nash, Budapest, advises that it is not known exactly what are the intentions of the Hungarian Minister of Finance as to the utilization of the natural gas in Transylvania, several million cubic yards of which have already escaped, but it is likely that before the end of the year the gas will be in use in one or more of the towns and industrial plants in the immediate vicinity of the wells. The gas-producing region comprises some 5,800 square miles, and the Government has so far put in over 20 wells, varying in depth from 1,000 to 3,300 feet. It is thought that the supply of gas will last for at least 50 years.

Eventually the gas will be brought to Budapest, although probably not for a few years. In any case, as soon as it appears that the public is to have natural gas placed at its disposal, there will be an immediate demand for meters, purifiers, pipes, valves, stoves, burners—in short, everything used in the exploitation of natural gas. There is no reason why American manufacturers, if they employ the proper methods, should not have the bulk of this business, as the American preëminence in this line of manufacture is generally recognized in this country. Everything points to the development of a large business. Manufacturers should send representatives to study the field and personally choose agents.

SWEDISH COAL SITUATION.

Consul Stuart J. Fuller, Gothenburg, reports that the threatened scarcity of imported coal, due to the labor troubles in England and the augmented demand owing to the lack of water for power, is bringing about increased activity in the Swedish mines in Skane, in the south of the Kingdom. The Skane coal is not suited for coke and is of inferior quality. It is conceivable that the labor troubles in England might affect the situation to an extent such that Sweden would have to look elsewhere for its supply, thus giving a possible opportunity for the introduction of American coal.

Coal constitutes nearly 10 per cent. of the total imports into Sweden. About one-fifth of this fuel is entered at Gothenburg, which port and Stockholm are the principal import places, Malmo and Gefle coming next. The total import for the last three years for which figures are available has been, in tons In 1907, 4,146,785; in 1908, 4,427,507; in 1909, 4,084,055. It was practically all from Great Britain. The kinds in 1909 were, in tons: Anthracite, 146,162; gas and coking, 263,749; smithy and nut, 300,258; steam coal, 3,352,943; miscellaneous, 20,943.

The production of coal in Sweden is less than 7 per cent. of the consumption of the country, the output in 1910 being 302,800 tons.

CORK TRADE OF THE UNITED STATES.

The cork-growing industry is being introduced experimentally into the United States by the Department of Agriculture. At Chico, Cal., the Bureau of Plant Industry has growing quite a number of cork-oak trees of various species that were secured by David Fairchild, the Department's agricultural explorer. The Bureau of Forestry is also conducting experiments near Pensacola, Fla., where the Cork-oak acorns have been planted, some of which are growing in the second year successfully.

Lacking a native supply, the United States purchases abroad nearly $6,000,000 worth of raw and manufactured cork, official statistics for the calendar year 1911 showing imports of unmanufactured cork wood or bark, valued at $3,819,651, and of cork manufactures worth $2,070,672, a slight decrease from the respective totals of $3,908,533 and $2,191,563 in 1910.

MALAYSIAN TIN EXPORTS.

The Federated Malay States Government Gazette gives the following table to show the weight of tin (tin exported in the form of ore having been taken at 70 per cent. of the gross weight of the ore) exported from the Federated Malay States during 1910 and 1911 (picul = 133 1/3 pounds):

	1910.			1911.		
	Tin.	Tin contained in tin ore.	Total.	Tin.	Tin contained in tin ore.	Total.
States.	Piculs.	Piculs.	Piculs.	Piculs.	Piculs.	Piculs.
Perak	109,867	311,468	421,335	97,835	339,504	437,339
Selangor	43,397	196,795	240,192	54,215	176,960	231,175
Negri Sembilan	121	34,576	34,697	90	29,140	29,230
Pahang	12,930	27,744	40,674	15,281	28,673	43,954
Total	166,315	570,583	736,898	167,421	574,277	741,698

SHARK'S LIVER OIL INDUSTRY PROPOSED.

Vice-Consul General D. Milton Figart, Singapore, Straits Settlements, states that it has been proposed to start in Malaysia a small export trade in shark's liver oil. This oil is refined in Europe and sold as cod-liver oil. In October the ocean sharks come into the lagoon, between the barrier reef and the atolls, to pair. At this time they can be speared in large number by people skilled in catching them. There are several species of these sharks and they ordinarily run from 7 to 15 feet in length. The girth of an ordinary shark is the same as its length, and an 11-foot shark would be 11 feet around the body. The liver of a shark of this size gives about 5 gallons of oil. The oil brings $73 a ton. The sharks are found in pairs and the harpooners try to kill the male first, in which case they are able to also spear the female, as it does not desert its mate.

BOOK REVIEWS

Transactions of the American Institute of Chemical Engineers. Vol. III (1910). 8vo., 411 pages. D. Van Nostrand Co., New York, 1911. $6.00.

Contents: Evolution of Portland Cement Processes, Chas. F. McKenna. Study of Materials in Chemical Engineering Chas. F. McKenna. Reports of the Committee on Chemical Engineering Education, F. W. Frerichs. Remarks on Chemical Engineering Education, F. W. Frerichs. Development of the Chemist as an Engineer, F. W. Atkinson. The Training of Chemical Engineers which Meets the Requirements of Manufacturers, M. C. Whitaker. Teaching Industrial Chemistry, A. H. Sabin. Commercial Manipulation of Refractory Elements for Incandescent Lamp Purposes, Ralph E. Myers. The Manufacture and Industrial Applications of Ozone, Oscar Linder. The Changes in Industrial Chemistry Caused by Electricity, E. R. Taylor. Notes on the Corrosion of Iron and Steel and its Prevention, G. W. Thompson. Protal; a New Product for Use in the Arts, F. G. Wiechmann. Chemical Industries of Canada, J. C. De Cew. Underground Waters for Manufacturing Purposes, Wm. M. Booth. Loss in Coal Due to Storage, A. Bement. Nitric and Mixed Acids, Schuyler Frazier. Plant Design, Wm. M. Grosvenor. The Fitzgibbon Boiler, J. Alexander. Manufacture of Hydrated Lime, R. K. Meade. Bleaching Oils with Fuller's Earth, David Wesson. SYMPOSIUM ON SEWAGE DISPOSAL. Principles of Sewage Disposal, G. C. Whipple. Sewage Disposal in Europe, Rudolph Hering. Sewage Disposal in New York City and Vicinity, G. A. Soper. Sanitary Conditions in their Relations to Water Supplies in the Vicinity of New York, N. S. Hill, Jr. Unsolved Problems of Sewage Disposal, C. E.-A. Winslow.

It speaks well for the activity of our youngest chemical society, that in the third year of its existence, it can produce such an imposing array of papers as the table of contents shows.

The volume, which shows the usual excellent work of the publishers, as well as evidence of careful proof-reading, contains much to interest not only the chemical engineer, but also the chemist who is not an engineer. The teacher of chemistry and the civil and the sanitary engineer will find much to interest them.

Aside from the papers on Chemical Engineering Education and allied subjects, all of which are of intense interest, the following are especially worthy of note:

Evolution of Portland Cement Processes, by Chas. F. McKenna.

The Manufacture and Industrial Applications of Ozone, by Oscar Linder.

Plant Layout, by W. M. Grosvenor and the Symposium on Sewage Disposal. D. D. BEROLZHEIMER.

The Technology of Bread-Making, including the Chemistry and Analytical and Practical Testing of Wheat, Flour and Other Materials Employed in Bread-making and Confectionery. By WILLIAM JAGO, F.I.C., F.C.S., AND WILLIAM C. JAGO. American Edition, Bakers' Helper Company, Chicago. 908 pages; 123 figs.

The present volume, as stated by the senior author in his preface, is a development of his previous works on the same subject which appeared in 1886 and 1895. The large amount of research in the field of bread-making since 1895 has caused the authors to make a complete revision of the earlier editions.

The general scope of the new volume and the relative importance which has been placed upon separate subjects are indicated in the following brief synopsis of the 33 chapters:

An elementary treatise upon inorganic and organic chemistry with special reference to ash, fat, carbohydrates, and proteids, 120 pages.

Enzymes, fermentation and the technology of yeast, 130 pages.

The chemistry of wheat, flour, and milling products, 150 pages.

The chemistry of bread and bread-making, 125 pages.

Nutritive value of bread and laws governing its sale, 50 pages.

Bake-house design and baking machinery, 100 pages.

Methods for analysis of flour, bread, confectioners' raw materials, etc., 220 pages.

Index, 15 pages.

In addition to the results of their own researches and experience, the authors have collected a wealth of material hitherto scattered in scientific journals, experiment station bulletins, court records, etc., of different countries and have added to this a great deal of information gathered from private sources. In reviewing the recent work in their field, the authors have prepared brief abstracts of all original articles which they have supplemented by a critical review. This method of treatment is particularly commendable and though the reader may not, in all cases, agree fully with the opinion of the authors upon some disputed points, he will find the arguments *pro* and *con* presented with equal fairness and fulness of detail.

In addition to its value to those specially interested in the bread-making industry this new volume will be of great service to the food chemist and public analyst. The chemist in preparing testimony for a court will find valuable assistance in the discussion of such topics as bread improvers, faulty bread, alum baking-powders, bleached flour, and scores of other subjects which might be mentioned.

The description of chemical methods is upon the whole very complete although the reader may, in certain cases, wish that in naming the author of a particular method the reference to the original publication had always been given for his guidance. The quartz wedge saccharimeter is used at present more extensively than the polarimeter in the analysis of food products and a short description of this instrument should have been included in the polariscopic methods of analysis.

The book is well printed and the cuts and photographs clear and distinct. C. A. BROWNE.

Die Chemie der trocknenden Oele. By WILHELM FAHRION. 8vo., pp. viii + 298. Berlin, Julius Springer, 1911. Price, 10 M.; cloth, 11 M.

The author calls attention to the fact that the greater importance of drying oils over all other forms of fatty bodies is indicated by the publication in 1867 of J. G. Mulder's work on "Die Chemie der Austrocknenden Oele" before the publication of any works devoted to the general chemistry of fats and oils.

The present work is a comprehensive review of the chemistry of drying oils brought well up to date. The principal part of the text is devoted to linseed oil, the other drying oils being very briefly treated.

In the present work, the literature of the subject appears to have been gone over very thoroughly, at least so far as it has been published in German or English, and reference is made throughout to the original papers. The subject is treated principally from the standpoint of the analyst, comparatively little material having been introduced from descriptions of manufacturing processes unconnected with analytical processes. To the analyst this work will be a convenient book of reference.

PARKER C. MCILHINEY.

NEW PUBLICATIONS

By D. D. Berolzheimer, Librarian, Chemists' Club, New York.

Analysis, Rapid Methods of —. By N. Samter. L. 8vo., 237 pp. $2.50. Halle, 1911. (German.)

Bread, The Chemistry of — Making. By J. Graut. 8vo. $1.25. London, 1912.

Cellulose, The Chemistry of—, with Special Reference to the Textile and Similar Industries. By C. G. Schwalbe. L. 8vo., 680 pp. $6.25. Berlin, 1912. (German.)

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Colloids, The— in Biologie and Medicine. By H. Bechhold. 8vo. $4.00. Theodor Steinkopff, Dresden. (German.)

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RECENT INVENTIONS

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

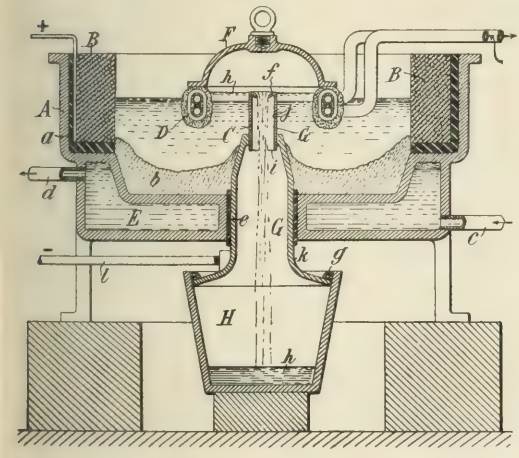
ELECTROLYTIC APPARATUS.

U. S. Patent No. 1,007,897, to G. O. Seward and F. von Kugelgen, Virginia.

This invention relates to an electrolytic cell or vessel for the production of metals lighter than their electrolytes.

In the production by electrolysis of those metals and alloys which have a less specific gravity than the molten electrolytes from which they are separated, a source of difficulty is the collection of the metals in such a way that they cannot come in contact with the gases set free at the anode, with which they would otherwise combine.

The present apparatus is designed to render possible and easy isolation of the separated metal or alloy by providing a combination of a cathode projecting up from the bottom of the electrolytic vessel through the electrolyte, and a chilled salt-incrusted collecting partition located above the cathode in such a way that the metal is confined as soon as separated and can be allowed to collect within the chamber or space bounded by such partition, from which it may be removed as convenient.



In the production of sodium, which remains fluid at the temperature of the electrolyte, difficulty is presented in discharging the metal from the cathode chamber into a suitable receiving vessel, by reason of the congealing of the metal upon the walls of the conduit which becomes clogged thereby.

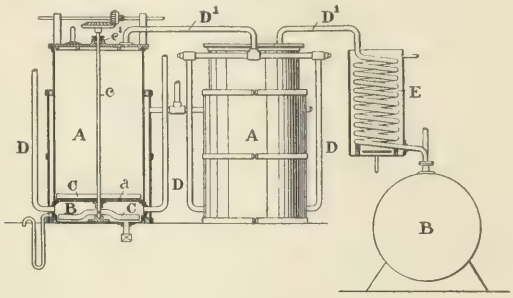
The invention provides for the ready discharge of such fluid metal by providing a vertical conduit into which the metal flows from the cathode chamber over a spout or lip which causes it to fall freely through the conduit without touching its walls, or touching only those portions of its walls which are adequately heated. This conduit is preferably formed integral with the cathode by making the latter hollow.

MANUFACTURE OF FERRIC OXIDE.

U. S. Patent No. 1,008,321, to John Gill, England.

This invention is based on the fact that calcium carbonate can be changed into a soluble calcium bicarbonate and in the presence of a solution of ferrous chloride precipitates the iron contained in the liquor as ferrous carbonate which is capable of being oxidized into ferric hydrate.

The invention consists essentially in treating waste or other liquors containing ferrous chloride with carbonate of lime and carbon dioxide and air to precipitate into ferric hydrate and subsequently calcining the ferric hydrate to drive off the water and obtain a pure or high-class oxide of iron.

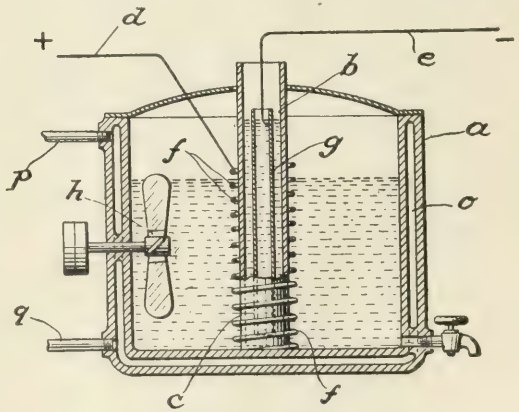


The accompanying illustration shows apparatus in which the process can be advantageously carried out.

PROCESS FOR CONVERSION OF LOWER OXIDS OF NITROGEN TO HIGHER OXIDS OF NITROGEN.

U. S. Patent No. 1,008,383, to Fin Sparee, Wilmington, Delaware. Assignor to the E. I. du Pont de Nemours Powder Co.

This is a method of treating oxides of nitrogen in solution to increase their oxygen content, which consists in passing a current of electricity through said oxides of nitrogen solution and acidulated water, between electrodes in the respective



solutions, the current density on the electrode in the oxides of nitrogen solution being above one hundred amperes to the sq. cm. and the current density on the electrode in the acidulated water below ten amperes to the sq. cm.

The accompanying illustration shows apparatus in which the process can be advantageously carried out.

MARKET REPORT.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF MARCH.

ORGANIC CHEMICALS.

Acetanilid	Lb.	20½	@	23
Acetone (drums)	Lb.	14½	@	15
Alcohol, grain (188 proof)	Gal.	2.56	@	2.58
Alcohol, wood (95 per cent.)	Gal.	50	@	52
Alcohol, denatured (180 proof)	Gal.	40	@	42
Amyl Acetate	Gal.	2.90	@	3.00
Acetic Acid (28 per cent.)	C.	1.87½	@	2.02½
Aniline Oil	Lb.	10¾	@	11½
Benzoic Acid	Lb.	23½	@	28
Carbon Tetrachloride (drums)	Lb.	9¼	@	12
Carbon Bisulphide	Lb.	nominal		
Chloroform	Lb.	20	@	30
Carbolic Acid (drums)	Lb.	18	@	19
Citric Acid (domestic), crystals	Lb.	38½	@	39
Camphor (refined in bulk)	Lb.	—	@	44
Dextrine (imported potato)	Lb.	5½	@	5¾
Dextrine (corn)	C.	2.95	@	3.31
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	14¾	@	15
Oxalic Acid	Lb.	7½	@	7⅞
Pyrogallic Acid (bulk)	Lb.	1.35	@	1.45
Salicylic Acid	Lb.	32	@	34
Starch (corn)	C.	2.20	@	2.50
Starch (potato)	Lb.	5	@	5¼
Tannic Acid (commercial)	Lb.	35	@	35½
Tartaric Acid, crystals	Lb.	30½	@	31

INORGANIC CHEMICALS.

Acetate of Lime (gray)	C.	2.25	@	2.30
Acetate of Lead (brown, broken)	Lb	7¾	@	8
Alum (lump)	C.	1.75	@	2.00
Ammonium Carbonate, domestic	Lb.	8	@	8¼
Ammonium Chloride, gray	Lb.	6	@	6¼
Aluminum Sulphate	C.	90	@	1.75
Aqua Ammonia (drums) 16°	Lb.	2¼	@	2½
Arsenic, white	Lb.	3½	@	3¾
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Barium Chloride	C.	1.45	@	1.60
Barium Nitrate	Lb.	4¾	@	5
Borax, crystals (bags)	Lb.	3½	@	4
Boric Acid, crystals (powd.)	Lb.	7	@	7½
Bromine, bulk	Lb.	25	@	30
Bleaching Powder (35 per cent.)	C.	1.25	@	1.30
Barytes (prime white, foreign)	Ton	18.50	@	22.50
Blue Vitriol	Lb.	4.90	@	5¼
Calcium Chloride	C.	65	@	90
Chalk (light precipitated)	Lb.	4½	@	6
China Clay (imported)	Ton	11.50	@	18.00
Feldspar	Ton	7.00	@	9.00
Fuller's Earth, powdered	C.	80	@	85
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1.15	@	1.55
Iodine (resublimed)	Lb.	2.60	@	2.65
Lead Nitrate	Lb.	8⅛	@	8⅝
Lithium Carbonate	Lb.	67	@	70
Magnesite (raw)	Ton	7.50	@	8.50
Nitric Acid, 36°	Lb.	3⅞	@	4¼
Phosphorus	Lb.	35	@	90
Phosphoric Acid, sp. gr. 1.75	Lb.	22	@	26
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bromide	Lb.	31	@	34
Potassium Permanganate (bulk)	Lb.	9¼	@	10
Potassium Cyanide (bulk) 98–99 per cent.	Lb.	19½	@	21
Potassium Iodide (bulk)	Lb.	2.10	@	2.15
Potassium Chlorate, crystals	Lb.	8¼	@	9½
Potassium Nitrate (crude)	Lb.	4¾	@	5
Potassium Bichromate, 50°	Lb.	6⅞	@	7
Quicksilver	Flask	46.00	@	48.00
Salt Cake (glass-makers')	C.	55	@	65
Silver Nitrate	Oz.	37	@	39
Soapstone in bags	Ton	10.00	@	12.00
Sodium Acetate	Lb.	4¼	@	5
Sodium Chlorate	Lb.	8¼	@	9½
Sodium Bicarbonate (English)	Lb.	2¾	@	3
Sodium Bichromate	Lb.	5	@	5¼
Sodium Hydroxide, 60 per cent.	C.	1.70	@	1.75
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent., spot	C.	2.20	@	2.22½
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	6⅞	@	7⅝
Sulphur, Roll	C.	1.85	@	2.15
Sulphur, Flowers (sublimed)	C.	2.20	@	2.60
Sulphuric Acid, 60° B.	C.	85	@	1.00
Talc (American)	Ton	15.00	@	20.00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	12¾	@	13
Tin Oxide	Lb.	47	@	51
Zinc Chloride (granulated)	Lb.	4¼	@	4½
Zinc Sulphate	Lb.	2¼	@	2½

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	40	@	45
Black Mineral Oil, 29 gravity	Gal.	12	@	12½
Castor Oil (No. 3)	Lb.	9½	@	10½
Ceresin (yellow)	Lb.	8	@	14
Corn Oil	C.	5.20	@	5.50
Cottonseed Oil (crude), f. o. b. mill	Gal.	34	@	35
Cylinder Oil (light, filtered)	Gal.	19½	@	20
Japan Wax	Lb.	9¼	@	9½
Lard Oil (prime winter)	Gal.	80	@	85
Linseed Oil (double-boiled)	Gal.	72	@	75
Paraffine Oil (high viscosity)	Gal.	23½	@	24
Paraffine (crude 120 & 122 m. p.)	Lb.	3	@	3⅛
Rosin Oil (first run)	Gal.	38	@	40
Spindle Oil, No. 1	Gal.	14	@	14½
Sperm Oil (bleached winter) 38°	Gal.	76	@	78
Stearic Acid (double-pressed)	Lb.	8¾	@	9⅛
Tallow (acidless)	Gal.	63	@	65
Tar Oil (distilled)	Gal.	30	@	31

METALS.

Aluminum (No. 1 ingots)	Lb.	19¼	@	19½
Antimony (Hallet's)	Lb.	7⅜	@	7½
Bismuth (New York)	Lb.	2.10	@	2.15
Copper (electrolytic)	Lb.	14.60	@	14.65
Copper (lake)	Lb.	14.65	@	14.75
Lead, N. Y	Lb.	—	@	4.05
Nickel	Lb.	40	@	45
Platinum (refined)	Oz.	45.50	@	46.00
Silver	Oz.	58¾	@	59⅜
Tin	Lb.	42⅜	@	43
Zinc	Lb.	6.85	@	—

FERTILIZER MATERIALS.

Ammonium Sulphate	C.	—	@	3.30
Fish Scrap, domestic, dried	Unit	3.25	@	10
Blood, dried	Unit	2.85	@	—
Tankage, high grade	Unit	2.70	@	10
Bone, 4½ & 50, ground, raw	Ton	27.00	@	—
Potassium, "muriate," basis 80 per cent.	Ton	38.05	@	—
Phosphate, acid, 16 per cent.	Ton	7.50	@	7.75
Phosphate rock; f. o. b. mine:				
Florida land pebble 68 per cent.	Ton	3.70	@	3.80
Tennessee, 68–72 per cent.	Ton	4.25	@	4.50
Pyrites, furnace size, imported	Unit	0.13	@	0.13¼
Castor meal	Unit	2.95	@	3.10 & 10
Mowrah meal	Ton	8.50	@	9.00

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume IV | MAY, 1912 | No. 5

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Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered at the Post-Office, Easton, Pa., as Second-class Matter.

ESCHENBACH PRINTING COMPANY, EASTON, PENNA.

TABLE OF CONTENTS.

EDITORIALS:

The United States Patent System ... 318

PATENT SYMPOSIUM:

The Inventor, the Public and the Law. By Walter F. Rogers ... 320
Patents and Chemical Industry in the United States. By B. Herstein ... 328
The Abuses of Our Patent System. By L. H. Baekeland ... 333

ORIGINAL PAPERS:

Some Recent Developments in Wood Distillation. By Thos. W. Pritchard ... 338
The Manufacture of Chloroform from Bleaching Powder and Ethyl Alcohol. By F. W. Frerichs ... 345
The Causes for Variations in Volatile Matter Determinations. By S. W. Parr ... 352
Monel Metal. By Richard H. Gaines ... 354
Free Lime in Portland Cement. By H. E. Kiefer ... 358
The Chemistry of Anaesthetics, IV: Chloroform. By Charles Baskerville and W. A. Hamor ... 362
Testing Methods of Rubber Contents in Raw and Vulcanized Rubber. By W. A. Ducca ... 372
The Volatile Acidity of Gum Tragacanth Compared with that of Indian Gum. By W. O. Emery ... 374
The Extraction of Potash and Alumina from Feldspar. By H. W. Foote and S. R. Scholes ... 377
A Colorimetric Method for the Determination of Carbon in Iron and Steel. By Jerome F. Kohout ... 378

LABORATORY AND PLANT:

The Distribution of Power in Portland Cement Manufacture. By Richard K. Meade ... 378
New Forms of Apparatus for Gas Analysis. By F. M. Williams ... 380

CURRENT INDUSTRIAL NEWS:

Tannery Wastes in Sewage ... 382
Scientific Methods in Earthenware Manufacture ... 383
The Decolorization of Sugar Juice with "Eponite" ... 383
The Prevention of Iron and Steel Corrosion ... 383
Lohmannizing ... 384
The Influence of Additions to Bronze ... 384
Copper Fungicides ... 384
The Utilization of the Potassium Content of Minerals ... 384
Purification of Water by Forced Oxidation ... 384
The "Chloride" Water Purification Process ... 385
The Serpek Process of Nitrogen Fixation ... 385
Diastafor in the Textile Industry ... 385
Wood Preserving ... 385
A New Filtering Material for Alkaline Liquids ... 385
Pumps ... 385
"Ratisal," a Trap Substitute ... 386
A Dry Fire Extinguisher for Electric Installations ... 386
A New Pattern in Spray Nozzles ... 386
The Digby and Biggs Dionic Water Tester ... 386
New Tank Valve ... 386

NOTES AND CORRESPONDENCE:

The Paint and Varnish Industry ... 387
Determination of Manganese in Steel. A Note ... 387
1. Apocynum or Indian Hemp, Rubber. By Charles P. Fox ... 387
Natural Gas ... 388
Natural Cement *versus* Portland Cement ... 388
Electric Production of Ferro-Tungsten ... 388
Bureau of Standards Analyzed Samples ... 388

BOOK REVIEWS:

"Rubber;" Paint Technology and Tests; Chemicals, Oils and Paints; Circular on Regulations for Illuminating Gas; Metallurgy of Iron and Steel; Casein, its Preparation and Technical Utilization ... 389

NEW PUBLICATIONS ... 391

RECENT INVENTIONS ... 393

MARKET REPORT ... 394

EDITORIALS

THE UNITED STATES PATENT SYSTEM.

Questions concerning "our patent system" are being discussed by the country as never before in its history. Always an inventive people, the number of our granted patents has exceeded a million; three of the last five years our exports exceeded our imports, and our industries have attained such magnitude that manufacturers exceed imports fifteen to one. For a large measure of this development we know and Emperor William of Germany assured the late W. F. Draper that our wise patent system is responsible.

In the Constitution of the United States, Art. 1, Sec. 8, Clause 8, we find that "Congress shall have the power—to promote the progress of science and the useful arts by securing for limited times, to authors and inventors, the exclusive right to their respective writings and discoveries." Pursuant to this constitution-authority the Federal Congress at once adopted patent laws. These were amplified in 1836, somewhat revised in 1870 and consolidated with the revised statutes in 1874, since when they have been in operation substantially unchanged.

The underlying principles of these laws are:

1. A man's thought, his conception, his invention, belongs primarily and necessarily to him. It may be kept a secret monopoly for generations and may be ultimately lost to the world.

2. The people desire to profit by new and valuable inventions; primarily by the inspiration and suggestive value in the publication of every new idea; secondarily by the birth and development of new industries, to preserve the discovery from loss, and ultimately to secure to the public the free use of the improvement.

3. Theoretically the people should not, and practically they cannot, take a man's idea, as by condemnation, without giving a fair return for its value. But, with the tender of a fair return, the people's right to secure the good of the community then justifies any means of penalizing a man's failure to give the public the benefit of the invention.

In harmony with these theories, first, the private property of the inventor is not attacked, is subject to no restrictions of working or compulsory license and should be protected by all the power of the law available in the protection of any other personal property. It is not in any sense a government granted monopoly; it was originally and might have remained the exclusive and private property of the inventor.

On the contrary, it is a revelation and inspiring suggestion on his part which he must be induced to make public for the inspiration and benefit of his fellow countrymen. Civilization cannot afford to lose the impetus which every invention gives to thousands of improvements, immediately following its publication. The benefit to the community of such prompt disclosure seems almost too obvious to require argument, though there may be here and there blind men who cannot see. Will modern capital undertake the development of a new industry under existing commercial conditions, requiring strenuous effort and expense without assurance of a fair security in its reward? No experienced manufacturer needs arguments to convince him that a real promise of large profit is required to induce him to experiment with his own fortune and his own business, to abandon established methods and set sail upon the uncharted ocean of experiment. No unprejudiced student of commercial history will question the enormous value to industrial progress of these voyages of discovery. Compare Holland and Switzerland when they had no patent system with the adjacent countries, Germany, France and Belgium having patent systems. Consider Siemens' failure to get a patent in Germany and his success in England that placed England a decade ahead of Germany in the steel business. The adoption by Switzerland of these methods and the industrial rejuvenation which followed, are insuperable facts. The industrial progress of a nation is proportionate to the completeness with which it protects its inventors. The United States offers the most perfect protection and has therefore made the most remarkable progress. Foreign countries, in modifying their systems as the results of experience, approximate ever more closely that of the United States. And, in the end, inventions must be preserved for free use of the public. It is contrary to intelligence to permit the entire loss of valuable arts, such as the manufacture of malleable glass by the Egyptians and the hard tempering of copper. History has shown that these are no mere arguments but actual conditions: causes and effects traced through centuries of experience.

But how may the people make a fair return in exchange for an idea? Our forefathers wisely recognized the enormous importance to the nation of securing its publication immediately. Mindful of centuries of experience under William Rufus and the early English kings, they shrewdly selected the only inducement which would lead the inventor to publish his inventions, would recompense him in proportion to the value of the property made public, would lead capital to assume the burden of exploitation, and yet would not only preserve the invention from being lost but tend to prevent indefinite secret monopoly and secure an early freedom of public use. So the people offered, as an adequate return for prompt and complete disclosure and for final appropriation of the invention as public property, to recognize the first inventor's exclusive right for a limited period.

The people of these United States, therefore, in their own interest came to the inventor with a proposal. As soon as the invention is completed, a full, clear and exact description such as will enable any one skilled in the art to carry out the invention, and exact claims of what is new and patentable together

with an oath that he is the first inventor, shall be submitted to the proper governmental department (Patent Office) together with a moderate fee for service in examination and publication. After careful examination by government experts and proper modification of statement so that the patent shall define the novelty and limitations of the invention, a patent shall be granted therefor, certifying the inventor's title, which patent to be constitutional should "secure to him the exclusive right to his discovery" and protect him before the courts in the exclusive right to make use of and sell *his* invention for seventeen years *after which it shall become public property.* Observe, it is his, but after reasonable recompense it is opened for public use. And if he use it secretly for an unreasonable period, or does not show due diligence in perfecting it and placing it before the public the people refuse to recognize his right in it; another may step in with the same invention, patent it, and compel the first inventor to pay royalty. Or if he publicly uses and sells it for two years without filing his patent application, the people refuse to recognize his special proprietary right and the invention becomes public property. This is certainly equivalent to condemnation. Thoughtless and ignorant people call a patent a government created monopoly. This is like some one's definition of a lobster as "a red fish that crawls backward," to which some wit replied "an excellent definition except that it is not a fish, it is not red, and does not crawl backward." A patent is not a monopoly in the ordinary sense but a limited recognition of ownership, the government did not create it (the inventor created it of the stuff that dreams are made of) and what the government *is* doing is arranging to equitably terminate the private ownership without discouraging the inventor.

This proposal of contract is very simple and virtuous in its simplicity. On the one hand it is based on the truth of the oath of the application and the novelty of the subject matter. On the other hand the fair offer is based on the fundamental wisdom of rewarding creative ingenuity, preserving progress and fostering industry. On the one hand it may be set aside by any proven falsity of oath of application by incomplete inaccurate statement and wholly or in part by lack of novelty. On the other hand everything that human ingenuity can devise to perfect and simplify procedure and eliminate needless expense in securing and maintaining patents for real inventions should be done, not merely "for the inventor" but more particularly for the nation—for ourselves. Consider the industrial stimulus to the nation, and the reduced cost to the consumer if we could make a patent absolutely certain for every true invention, and unquestionable when issued. Hundreds of inventions that are now poorly protected and therefore worthless to any one in particular would be developed into industries. Hundreds more that are still-born in the struggle of poverty would be added to the sum of individual achievement and national prosperity.

You may lead a horse to water but you cannot make him drink. It may be true that "the inventor is an eccentric individual who cannot help inventing" but the experience of centuries has shown that he is quite capable of secreting his invention, of letting it die with him if necessary rather than giving it to the public. The prosperity of a nation consists chiefly in the profitable employment of its labor to better productive advantage than that of other countries. This prosperity is based upon the stimulation of that productive effort we may call invention, *i. e.*, the discovery of new and valuable products and better machines and processes for the creation of value. To this end we must offer the inventor no mean or uncertain inducement to insure the disclosure of his invention, and the capitalist a fair security for investment and time for its proper development.

Having made such a bargain it is to the vital interest of every one of us to see that the public side of this contract is adequately carried out. In the fullest sense of the word, every attack upon the title of the inventor is a retro-active attack upon ourselves. Every stumbling block placed by public practice in his path is a stumbling block to our own success. His patent must have value to him and to do so must have a money value to the manufacturer. Limitation of the right which has wisely been granted him is not so much a shameful breach of faith on the part of his countrymen as a piece of arrant stupidity that kills the goose that lays the golden eggs. The simple logic which induced and created the original contract, commands us to maintain the wise policy and to see that it is equitably and justly enforced, with the least possible delay, error and expense.

What we need is not new patent laws. Those we have are admirable—perhaps the best in the world—incomparably better than numerous misbegotten bills, conceived in ignorance and sired by demagogery, offered to Congress with the hope of catching the socialistic vote by a flimsy pretense that such bills are "anti-monopoly" or "anti-trust," whereas they are in fact recklessly destructive of our best socialistic laws, our most anti-monopolistic laws—the patent laws. The private monopoly of inventive creation can be overcome only by just reward. What we need is better administration of the very excellent laws we now have, better provision for the service that is paid for in the Patent Office instead of misapplication of these funds to other uses, more study of the good principles we have instead of carping criticism of the evil results of our own cherished administration of fundamentally good laws. We need a court that shall apply our laws consistently instead of bandying these seeds of our national prosperity from district to district across the land to drop them sterile in the stony places of litigation—a court that shall be competent to sift and judge the issues involved instead of confessedly drawing lots—ignorance in one hand and bewilderment in the other. And after such, amendment of our procedure, after due consideration, possibly some cautious strengthening of our present law the better to secure for the nation the fullest inventive service by better securing to the inventor his temporary reward.

And this is distinctly *your* affair. You suffer by the delay and uncertainty of industrial progress and you pay the bill. These are the absolute certainties in any case. Your life is shortened by delaying the world's progress while you live. If the inventor of a new plastic is delayed in establishing his rights in certain fields, little or no money will be spent in those fields until the doubt is cleared up. If patents on a protective coating for concrete can be fought through one district after another for years the money required for new plant to meet your demand or inform you of its usefulness will not be invested on an uncertainty until the first law of self-defense is satisfied. If the patents on a new way of making sulphuric acid, after having been secretly operated for ten years, are so issued to opposing interests that they overlap and the manufacturers have to spend years in fighting out questions of title, you have to wait for the progress of the industry and all its numerous dependencies. If enormous capital is permitted to drag out interference and infringement suits, whether justified or not, to the impoverishment of the independent inventors and competitors, you not only have to get along without the improvements and economical devices but you pay the bill. It all goes into the selling price whether it sneaks in through the back door of manufacturing cost or boldly marches in the front door of patent account written off. If it costs one inventor $60,000 to fight his interference suits, it costs the other side about as much and whichever wins, you pay the bill as soon as he can make you—lucky if you don't have to pay the loser's expenses too, either on the next thing he succeeds in making or by the way of the bankruptcy court. And you pay every moment of the day. Bed-springs, bath-tubs, soap, safety razors, wash-cloths, underwear, toilet articles, shirts, collar buttons, breakfast foods and dishes, carriages, automobiles, train and car service, safety devices, elevators, office fixtures, typewriters and copying machines, stationery, pencils, pens and printing methods; every convenience or economy of the business day and every evening amusement brings you its little bill augmented by this cost of litigation and delay.

You can help correct the loose and wasteful administration of a wise policy. You can give a little time and thought and above all *enthusiasm* and *purpose* to the spreading movement for correction. You can call the attention of manufacturers, purchasing agents, proprietors, or stockholders to the movement, giving them the articles published in this issue of THIS JOURNAL. Make them write to their congressmen. Certainly you can write a note to the congressman from your district and to each of the Senators from your state, "putting it up to him hard" that the patent law we have is of inestimable value to the country—its best bulwark against mere money power or ordinary monopoly, that subversive changes of the law must not be tolerated but that the practice should be simplified and clarified so that the law itself stands clearly forth. Tell him how many thousands of dollars worth of patented goods you make, or use, or sell per year (and you will be amazed if you figure it out) and tell him how many people you employ who are dependent for their livelihood on this work. And you can bring the matter before your business or technical associations and pass resolutions to the President.

The average citizen feels that this patent situation is not a matter of concern to him, but a careful analysis of the underlying principles and conditions shows that it is a matter of vital interest to the inventor, the manufacturer and the consumer—to every man, woman and child in every quarter of the nation.

W. M. GROSVENOR.

PATENT SYMPOSIUM

THE INVENTOR, THE PUBLIC AND THE LAW.[1]

By WALTER F. ROGERS.

I am here to-night, not officially, but as a member of the patent bar of Washington and New York. Your managers believe that my professional views are modified and in a measure directed by association work. My own idea is that generally the patent lawyers are doing representative work, and that on the whole they candidly urge the views of all—the inventor, the mechanic, the manufacturer, the combination, the public. As there are comparatively few combinations, the majority of us speak for the individual, but we do not condemn unheard the combinations, because we expect or desire them to be controlled and utilized in the interest of the public without interference with their right to a fair profit.

I am told that all these classes of men are here or represented here to-night, and in what I shall have to say I follow the hint of some of your committee. They tell me that one-third know all about patents and that two-thirds do not.

Having in mind *also* the "remnant," the one-third, I propose to discuss not only the relations of the inventor and the public and the law to each other from an experience and study covering some thirty years—in the Patent office, the law school and in practice, but also to put it before you as I see it colored by the vital problems of to-day.

For a year or two the hundreds and thousands of individuals, of small and medium shops and plants based on patents, have been forgotten in the fierce discussion of the few great corporations, combinations and trusts owning patents, and the many are now endangered by the swarm of ill-considered and hastily devised remedies intended for the few. The truth is that the problems of to-day are in their broad aspects, though in other forms, the same problems which England dealt with nearly three hundred years ago. Let us see what relation the inventor and the

[1] Paper presented at the joint meeting of the Am. Chem. Soc., Am. Electrochemical Soc., and the Soc. of Chem. Ind., New York, April 19, 1912.

public then bore to each other—and to monopolies—and what is their relation to-day.

The patent system of the United States is a development of the older system of Great Britain, with, however, fundamental differences.

The British system arose from a negative provision in the Statute of Monopolies, 21 Jac. 1 (1624), based upon common law precedents, especially excepting from a sweeping prohibition of monopolies those granted for a term of years to the importers of a new art or trade and those granted to the "first inventor" of "new manufactures" for a term of fourteen years. The patent system of the United States rests upon a positive provision of the Constitution, having a broader aim and a markedly different origin and expression of method.

There is in the books and in the minds of many historians a certain misapprehension of the origin of the British patent law. It was Parliament which first endeavored to sustain monopolies—the trade monopolies of the town guilds. The concentrated power of the guilds controlled Parliament through their representatives. The Crown, in the first instance, granted monopolies under a salutary principle. The privileges and charters and patents were then granted by the Crown for the purpose of introducing new arts and trades from abroad into the country, so that the workmen who could not get employment in the trades because they were not members of the Guilds might receive employment under the new arts and crafts, and the new trades. The result, however, was such an extension of the privileges granted by the Crown that they soon became abuses, far greater abuses than were the Guilds. They were made the basis for extortion and shameless revenue-producing trickery. The common law courts constantly strove to hold even the scales of justice between the royal privilege and Parliament as representing the Guilds. It is to their eternal credit that the courts evolved and bravely maintained, as far as possible, the doctrine which holds to-day as the true one.

It is not necessary in an assemblage of this sort to detail the rising of the English people against this oppression of privilege of the "system." At the beginning of the 17th century Elizabeth realized that the matter had reached the danger point. She issued her famous proclamation, and her Secretary, Cecil, wrote the Parliament in words so aptly descriptive of the times and thoughts of men that a part of his letter needs to be quoted:

"I dare assure you from henceforth there shall be no more granted, they shall all be revoked. And because you may eat your meat more savoury than you have done, every man shall have salt as good and cheap as he can buy it or make it without danger of that patent which shall presently be revoked. The like benefit shall they have who have cold stomachs both for *aqua vitae* and *aqua composita*, and the like; and they that have weak stomachs, for their satisfaction, shall have vinegar and alegar, and the like, set at liberty. Train oil shall go the same way, oil of blubber shall march in equal rank; brushes and bottles endure the like judgment. The patent for pouldavy (sail cloth) if it be not called in, it shall be. Woade, which, as I take it, is not restrained either by law or statute, but only by proclamation (I mean from the former sowing) though for the saving thereof it might receive good disputation, yet for your satisfaction the Queen's pleasure is to revoke that proclamation; only she prayeth thus much, that when she cometh on progress to see you in your counties, she be not driven out of your towns by suffering it to infect the air too near them. They that desire to go sprucely in their ruffs may, at less charge than accustomed, obtain their wish. The patent for starch which hath been so prosecuted shall now be repealed."

The House, filled with joy, sent a committee to call upon the Queen and express their thanks, and on November 30, 1601, the leader of all feminists made her celebrated "Golden Speech" in which occurred, among many other similar statements, the following:

"Mr. Speaker, you give me thanks, but I am more to thank you, and charge you to thank them of the Lower House from me; for had I received knowledge from you, I might a'fallen into the lapse of an error, only for want of true information.

"Since I was Queen, yet did I never put my pen to any grant but upon pretext and semblance made me, that it was for the good and avail of my subjects generally, though a private profit to some of my ancient servants, who have deserved well; but that my grants shall be made grievances to my people, and oppressions, to be privileged under color of our patents, our princely dignity shall not suffer it.

"When I heard it, I could give no rest unto my thoughts until I had reformed it, and those varlets, lewd persons, abusers of my bounty, shall know I will not suffer it."

The Queen's bench soon had an opportunity to pass upon the principle. The leading and familiar case is Darcy v. Allein, 11 Coke, 84 b. Abridged, 1 Brodix Patent Cases, 1. (See also Darcy v. Allin, 1 Web. P. C.)

The arguments of counsel in that case is given in Noy, 173.

"Now, therefore, I will show you how the judges have heretofore allowed of monopoly—patents—which is that when any man by his own charge and industry, or by his own wit or invention doth bring any new trade into the realm, or any engine tending to the furtherance of a trade that never was used before; and that for the good of the realm; that in such cases the kings may grant to him a monopoly—patent for some reasonable time, until the subjects may learn the same, in consideration of the good that he doth bring by his invention to the commonwealth, otherwise not."

It will be seen that the common law had thus provided an adequate remedy against monopolies. It classed as unlawful, monopolies of existing arts and trades but recognized the propriety of purchasing the introduction of new trades and manufactures by granting a monopoly for a limited term. Though legislation subsequently became necessary, it was not to supply a deficiency in the law, but to reassert the law which was being evaded and defied.

You all, of course, whether lawyers or not, know that the great name in law of those days is Coke. Sir Edward Coke had been the law officer in the cited playing-card monopoly case of Darcy v. Allein. He defines "monopoly" in terms which have been significantly paraphrased in recent decisions of the courts of the United States, nearly three hundred years later. In his famous Institutes (**3**, 181) he says:

"A monopoly is an institution or allowance by the King; by his grant, commission, or otherwise, to any person or persons, bodies politic or corporate, of or for the sole buying, selling,

making, working, or using of anything whereby any person or persons, bodies politic, or corporate, are sought to be restrained of any freedom or liberty that they had before, or hindered in their lawful trade."

It is probable that if Elizabeth had been succeeded by one of equal capacity and of the same intense pride in her people the matter might have been concluded, but as ever with the King and the commoner alike, the necessities of the exchequer drove James and Charles to permit and even encourage excesses under their primarily praiseworthy endeavors to follow Elizabeth in giving a national character to the various trades.

Keeping in mind how bitter was the fight, how bitter the protest and the sense of personal and national outrage engendered by these monopolies, it is of prime significance that Parliament, when it enacted the Statute against Monopolies in 1624, made that notable exception in Section 5 in favor of the introduction of a new trade and that pregnant exception in Section 6, in favor of new inventions. Let us once more read Section 6, keeping in mind the fact that the whole nation was aroused against monopolies and that nevertheless the nation realized the necessity of maintaining two forms of monopolies which they understood could best serve to check the general monopolies. Now this is the way the statute read upon which the patent and trade laws of Great Britain have rested from that time to this, the patent law remaining without amendment until 1835.

"Provided also and be it declared and enacted, that any declaration before mentioned shall not extend to any letters-patent and grants of privilege for the term of fourteen years or under, hereafter to be made, of the sole making or working of any manner of new manufactures within this Realm, to the true and first inventor or inventors of such manufactures, which others, at the time of making such letters-patent shall not use, so also they be not contrary to law or mischievous to the State, by raising prices of commodities at home, or hurt to trade, or generally inconvenient; the said fourteen years to be accounted from the date of the first letters-patent or grant of such privilege hereafter to be made; but that the same shall be of such force as they should be, if this act had never been made, and of none other."

Observe the purpose, *not* so much to encourage and protect the original inventor, as to encourage the introduction of the new manufacture into the realm, and that the granting of the patent remained an exception, and was and is by the favor of the Crown.

Hapless Charles I., driven by his money necessities, went himself into business on a reckless scale. The result was the creation of the infamous national monopolies of glass, starch, salt, cloth-finishing, alum, soap, etc.

The licenses and holders of charters and benefits and their inspectors were vehemently and on every hand charged with extortion and blackmailing, the most offensive form of house-searching and exactions, and with bringing malicious suits and causing ruinous delays for the purpose of squeezing the "consumer."

Clarendon, in his History of the Rebellion, states the result, the practice and the failure, briefly thus:

"Projects of all kinds, many ridiculous, many scandalous, all very grievous, were set on foot; the envy and reproach of which came to the king, the profit to other men, insomuch as of £200,000 drawn from the subjects by these ways in a year, scarce £1,500 came to the king's use and account."

Finally, Pym in his immortal speech in Parliament in 1640, condensed the complaint against the abuses by the court of the favors of the Crown and placed the monopolies first on his list of grievances. It was in this debate that Colepepper is credited with the following speech relating to the practices of the inspectors and licensees when enforcing the charters and grants of the Crown, a speech commended as a pointer to certain legislators and editors.

"These men, like the frogs of Egypt, have gotten possession of our dwellings, and we have scarce a room free from them. They sup in our cup, they dip in our dish, they sit by our fire; we find them in our dye-vat, washbowl, and powdering-tub; they share with the butler in his box, they have marked and sealed us from head to foot. They have a vizard to hide the brand made by that good law in the last Parliament of King James, they shelter themselves under the name of a Corporation; they make bye-laws which serve their turns to squeeze us and fill their purses."

Then when the common law had been evaded and defied and when the statute accepted by the ruler had been rendered practically nugatory by the abuse of the royal privilege, came the revolution which for all time confirmed both the letter and the spirit of the statute.

The Statute of James I., the Statute of Monopolies, came over in the Mayflower with the pilgrims, and the patents granted by the General Court of Massachusetts first recognized the principle of originality, for they granted the monopoly for certain inventions forbidding others to use such articles unless they were different from those of the patentee.

I think no one can look upon a waving field of wheat or a meadow of rustling grass without picturing the reaper swinging his scythe in the sun. To "patent" men this brings to memory John Jenks, who in 1646 received a patent in Massachusetts for the improvement over the short, thick, straight English scythe, of the longer, thinner, curved implement with stiffened back, still in use, and which for so many generations cut and gathered the grains in the fields of our forefathers.

This idea of granting patents for new inventions prevailed in that and other colonies. When the Constitutional Convention met, they had before them and under consideration the English idea and a suggestion of a different idea in the practice of the colonies. The English idea had been to encourage monopolies so that the *introduction* of a new trade or a new art was the essence of the law. The constitutional idea, however, was that of encouraging domestic invention, and in the first patent law of 1790, and in all the subsequent amendments of that law, the basic idea has been to encourage original invention. The introduction of those inventions into use was wisely left to

he incentive of business enterprise. The intention was to encourage inventive thought, to secure a disclosure of the inventive thought as promptly as possible. Evidently, it was not deemed wise to require that the inventive thought, which might be years in advance of the day, should be withheld until the inventor had been able to make provision for actually introducing the manufacture. The sooner the inventive thought was disclosed the sooner it became public property. The sooner the inventive thought was disclosed the sooner it would be an incentive to others to improve upon that inventive thought. It was intended to offer the strongest incentive for a prompt application and disclosure. Inventors were to be made to feel the necessity of promptly completing their inventions and this they could do either by actually reducing to practice the invention or by filing an application for a patent. They need not provide, in advance, for the manufacture, or the trading.

When it is conceived that the essential spirit of the constitution and the patent law is to benefit the public by securing a disclosure, it is clear that the disclosure should be prompt and complete.

When the inventor has disclosed his invention, that is to say, when the patent is granted and the disclosure is given to the public, he has done all that he is required to do. He has completed his bargain. This it is which has distinguished the laws of the United States for over one hundred and twenty years from the majority of other patent laws, and it is this spirit which has been recognized by all the world as the ideal spirit of patent law. All provisions of working, taxation, compulsory license have an essentially different purpose. Primarily they were either revenue provisions, or the equivalent of tariff provisions. The consistent history of the English patent law has been that of a trade law, and all her restrictive provisions have been, in effect, tariff provisions. The same is true of Canada, where the majority of applications are filed by our citizens. In the continental countries of Europe such provisions of law have been written with an eye to revenue and are now maintained under vigorous protest primarily by a class of interested people who have in mind the additional fees.

The English law, while primarily a trade law, served also by interpretation to foster and encourage invention. All things considered, there is no more impartial tribute than that of *Bentham* in "*Rationale of Rewards*," p. 92.

"It is an instance of a reward peculiarly adapted to the nature of the service and adapts itself with the utmost nicety to those niceties of proportion to which it is most difficult for reward, artificially instituted by the legislature, to confer. If confined, as it ought to be, to the precise point in which the originality of the invention consists, it is conferred with the least possible waste of expense. It causes a service to be rendered, which, without it, a man would not have a motive for rendering; and that only by forbidding others from doing that which, were it not for that service, it would not have been possible for them to have done. Even with regard to such invention, for such there will be, when others besides him who possess the reward have scent of the invention, it is still of use by stimulating all parties and setting them to strive which shall first bring the discovery to bear. With all this it unites every property that can be wished for in a reward. It is variable, equable, commensurable, characteristic, exemplary, frugal, promotive of perseverance, subservient to compensation, popular and reasonable."

(Quoted by Godbolt, 252, and Coryton, p. 37.)

Our patent laws express in the form of statutes the purpose of the legislators when dealing with a form of property of which the striking feature is, *that the public is to be the legatee.*

All law is complicated by the bewildering variety of facts and conditions, by the difficulty of getting at the truth; but the patent law is in its fundamentals clear and simple.

There must be first the *disclosure* of a new idea of a means or method useful in a practical art and not obvious even to those skilled in the art. The disclosure is by means of an application, and the utility and novelty are determined by an examination in which the application must run the gauntlet of all prior knowledge or prior use in this country, and all prior patents and publications, of any domestic public use or any publication more than two years prior to the application; and the possibility of meeting a rival who has already occupied the field, or of being stopped by the applicant's previous negligence or concealment or by a foreign patent dating back more than twelve months.

When the application is allowed he has a period of six months in which to pay the final fee or he may let his application become forfeited and then renew within two years, subject, however, under a recent ruling, to have his right to renew taken away by the activity of some rival who enters the field in that time. Moreover, the principle of this rule obtains now in the courts in the consideration of a patent. Then after the patent is granted it is still open to question. It is only *prima facie* valid. The patentee has little hope of ever securing damages, but if he has a good patent is practically certain of enjoining an infringer, *provided* he has the capital to conduct the suit.

The law provides also that the patentee may, under conditions precedent of the statutes, amend his patent to more accurately describe the illustrated invention or to limit his claim, and may even reissue to enlarge his claim to include the idea of means or method which he had illustrated and described and which he had intended to claim, *provided* he established these propositions and *provided* he has been reasonably diligent in applying for the reissue and is not held to have expressly or by circumstances dedicated to the public the matter not claimed in the original patent.

The patentee may hold as infringers all who employ substantially his idea of means or method, *if* the claim of his patent be broad enough to cover the idea and *if* he is entitled to such a claim. Thus is the limited grant of exclusion offered the inventor, nicely balanced by the many obstacles and restrictions. But there are additional features which seem to tip

the scale down far toward the public's more selfish interest.

As the law *now* stands, if a patentee has maintained his patent in eight circuits of the United States and one circuit should find his patent invalid or should find that some one manufacturing a similar device is not an infringer, then his rival may make the thing in that circuit and sell it in all the other eight circuits.

It is obvious that a great combination whose work is based largely upon patents may easily prosecute its applications in the most approved manner, make validity searches and carry through elaborate and expensive interferences and infringement suits. It may also easily comply with any requirements which demand expenditure of capital or effort.

Because some of these combinations do, as thousands of individuals are obliged to do, put into their safes some of the patents they have and decline to manufacture, it is proposed to provide compulsory license and compulsory working and taxation and various other burdensome requirements which can so easily and readily be met by these combinations, and which it would be most difficult for the average inventor to meet.

The average inventor loses a large part of the life of his patent because he is in advance of the time, because he cannot interest the public, or because he finds it difficult to secure the necessary capital, and sometimes from sheer negligence or inertia.

What is the contract with the patentee? What are his rights?

There has never been any doubt in the minds of the courts of the property right of a patentee. Chief Justice Taney, speaking for the Supreme Court in *Bloomer v. McQuewan*, 14 How. 539, 549, said:

"The franchise which the patent grants consists altogether in the right to exclude every one from making, using or vending the thing patented, without the permission of the patentee. This is all that he obtains by the patent."

Again Mr. Justice Peckham in *Bement v. National Harrow Company*, 186 U. S. 70; 46 L. Ed. 1058, speaking for the Supreme Court, said:

"It was, therefore, the owner of a monopoly recognized by the Constitution and by the statutes of Congress. An owner of a patent has the right to sell it or keep it; to manufacture the article himself or to license others to manufacture it; to sell such articles himself or to authorize others to sell it. As stated by Mr. Justice Nelson, *in Wilson v. Rousseau*, (4 How. 646, 674), in speaking of a patent:

"The law has thus impressed upon it all the qualities and characteristics of property for the specified period; and has enabled him to hold and deal with it the same as in the case of any other description of property belonging to him, and on his death it passes, with his personal estate, to his legal representative, and becomes part of the assets.'"

One of the older cases is *Grant v. Raymond*, 6 Pet. 218, 241, in which the Court said:

"And it cannot be doubted that the settled purpose of the United States has ever been, and continues to be, to confer on the authors of useful inventions an exclusive right to their inventions for the time mentioned in their patents. It is the reward stipulated for the advantage derived by the public for the exertions of the individual, and is intended as a stimulus to those exertions. The laws which are passed to give effect to this purpose ought, we think, to be construed in the spirit in which they have been made; and to execute the contract fairly on the part of the United States, where the full benefit has been actually received; if this can be done without transcending the intention of the statute, or countenancing acts which are fraudulent or may prove mischievous. The public yields nothing which it has not agreed to yield; it receives all which it has contracted to receive. The full benefit of the discovery, after its enjoyment by the discoverer for fourteen years, is preserved; and for his exclusive enjoyment of it during that time the public faith is pledged."

Again in *United States v. American Bell Telephone Co.*, 167 U. S. 224; 42 L. Ed. 144, the Court said:

"The only effect of it was to restrain others from manufacturing and using that which he invented. After his invention he could have kept the discovery secret to himself. He need not have disclosed it to any one. But in order to induce him to make that invention public, to give all a share in the benefits resulting from such an invention, Congress, by its legislation, made in pursuance of the Constitution, has guaranteed to him an exclusive right to it for a limited time; and the purpose of the patent is to protect him in this monopoly, not to give him a use which, save for the patent, he did not have before, but only to separate to him an exclusive use. The Government parted with nothing by the patent. It lost no property. Its possessions were not diminished. The patentee, so far as a personal use is concerned, received nothing which he did not have without the patent, and the monopoly which he did receive was only for a few years."

In the comparatively recent case of *Continental Paper Bag Company v. Eastern Paper Bag Company*, 210 U. S. 405, Mr. Justice McKenna quoted the above case as follows:

"Counsel seem to argue that one who has made an invention and thereupon applies for a patent therefor occupies, as it were, the position of a quasi-trustee for the public; that he is under a sort of moral obligation to see that the public acquires the right to the free use of that invention as soon as is conveniently possible. We dissent entirely from the thought thus urged. The inventor is one who has discovered something of value It is his absolute property. He may withhold a knowledge of it from the public, and he may insist upon all the advantages and benefits which the statute promises to him who discloses to the public his invention."

Mr. Justice McKenna then continued:

"And the same relative rights of the patentee and the public were expressed in prior cases, and we cite them because there is something more than the repetition of the same thought by doing so. It shows that whenever this Court has had occasion to speak it has decided that an inventor receives from a patent the right to exclude others from its use for the time prescribed in the statute. 'And for his exclusive enjoyment of it during that time the public faith is forever pledged.' (Chief Justice Marshall in *Grant v. Raymond*, 6 Pet. 243, p. 242.)"

Many circuit courts of appeals have spoken to the same effect. One which cites numerous authorities is *Rubber Tire Wheel Co. v. Milwaukee Rubber Works Co.* (C. C. A.), 154 Fed. Rep. 358.

"Under its constitutional right to legislate for the promotion of the useful arts, Congress passed the patent statutes. The public policy thereby declared is this: Inventive minds may fail to produce many useful things that they would produce if stimulated by the promise of a substantial reward; what is produced is the property of the inventor; he and his heirs and assigns may hold it as a secret till the end of time; the public

would be largely benefited by obtaining conveyances of these new properties; so the people through their representatives say to the inventor: Deed us your property, possession to be yielded at the end of 17 years, and in the meantime we will protect you absolutely in the right to exclude every one from making, using or vending the thing patented, without your permission."

Note that the right granted the inventor is not the right to make, use and sell the invention. He had that at common law. It is the right to exclude others from making, using or selling for the limited term of his monopoly. But now it is proposed to permit any one who looks with a longing eye upon the invention to insist upon a license however hurtful or ruinous—and to clip and trim the already limited grant of exclusion by requirements impossible of performance by the average patentee, however energetic or earnest. The great majority of patentees want nothing so much as to see their inventions in use.

By these proposals, if they should become law, no matter how near the goal, he may see all his hopes slip away into the hands of rivals who have given nothing to the public, into the hands of the very combinations his invention would ultimately have checked. It is not the Constitution we followed. It is not the law we adopted. It is not the bargain we made. It is not the policy which has studded every county, town and hamlet with thriving independent shops and plants—with industries which never could have begun or lived but for the protection of the patent law. The effect of such laws, if adopted, will be to benefit the very combinations at which the bills are aimed. They may easily follow the onerous provisions—and may harass every individual, under the protection of the law.

The inventor will then find it still harder to secure capital. As it is now, the law enables him to get his patent in advance even of the demand. He seldom can interest capital until he has his patent; but under such provisions the most friendly capital will not take the risk of having to meet the burdensome and harassing litigation certain to be thus imposed. The litigation now required to maintain a patent is certainly sufficient without imposing this most vexatious of all forms of litigation.

In addition to the general objections which have been suggested there are many specific objections. For example, the proposed bills do not take into account the endless and burdensome outlay put upon manufacturers who have numerous alternate structures devised by various inventors employed at high salaries. They do not take into account the effect of the certainty of a reduction in the number of inventions produced and patented. They do not take into account the probable confusion of the rights of co-workers, licensees, territorial grantees, etc. They do not take into account the entirely incommensurate relation of the penalty to the offense. They do not take into account in referring to foreign countries the countries which provide for far greater protection under their patents than does the United States, protecting substitute structures as well as the main one, a provision not practicable nor wise in this country. They do not take into account the fact that the practical application of compulsory license and working clauses has been a constant source of friction and oppression in foreign countries, nor that the actual working of these clauses has resulted in benefits to the privileged classes in foreign countries and has made the patent laws a smaller factor in the industrial progress of those countries than they have been in this country.

The citation of other countries is no argument. Even if it could be shown that similar laws had been of some advantage to those countries, the conditions are not the same—the purpose is not the same. We have no centralized, compact, trading country. We are a far-flung democracy with a tremendous interstate and interstate commerce. We have no special classes to serve—and no near and more powerful neighbor to fight that can not be met by our tariff laws.

I know of no more amazing instance than this project of men who are fighting the tariff, and special interests and monopolies; than these proposals, whose inevitable result must be to cripple and bind the very concerns, the individuals and the independent shops, who, protected by their patents, are enabled to exist and thrive to the benefit of the public and in the face of the combinations.

But for the patent laws there would, probably, be but one printing press company, but one typewriter company, but one electric company, but one adding machine company—but one of many now listed in the thousands. Where there is now one combination there would be scores.

Thus, historically and traditionally and by the interpretation of the courts, the spirit of our patent laws is that of an untrammeled grant of exclusion. It is that spirit which has informed our laws and has made them so successful in practice. It would be an archaic and reactionary step to inject into such a system the mere trade principle of compulsory license or compulsory working. There is, however, a further objection, inherent in the nature of the property and in the essence of the property right.

The inventor has something which he may keep secret. He need not divulge his secret. He may, if he chooses, employ his invention in some practical art. But no one, no law, can force him to make, use or sell the thing which is the subject matter of his invention. He is, however, at the mercy of any one who discovers his secret and therefore is generally willing to accept the proposition of the Government that he shall divulge his secret, that he shall disclose it by means of a patent. When he is asked to disclose this invention he is promised a reward. He is not promised that he shall have a right to make, use or sell the invention. He has that always. He had that by the common law. He had that as a natural right. The bargain is, as I have said, that he shall have the right to exclude others from making, using or selling the invention. There can be no possible limitation upon the grant of exclusion within the terms of our laws and within the spirit of the Constitution.

Viewed in any way, the enactment of such laws will mean simply this, that the term of the patent will be limited, that is, when the government says to the inventor at the end of two or three or four years, you must grant a license to any one who asks for it or to any one whom a bureau official or a court thinks should have it, or you must work your invention or lose the patent, that is simply, in effect, limiting the term of the patent to that time and putting a ruinous burden on all, *excepting those favored few who with great capital are enabled to in some manner work many patents and to vigorously contest all applications for licenses.*

Such a provision is also, on its face, a temptation to oppression, a temptation to perjury, and in its practical workings would put into the hands of the bureau official with no experience whatever in the property rights involved in patents, the settlement and disposition of those property rights; and if the jurisdiction be given a court invites additional litigation, which will be only a guessing contest.

I have spoken hitherto of some of the difficulties of securing and maintaining a patent. The Commissioner of Patents has to do only with that side of the matter which relates to the grant of the patent. The far greater field is in the consideration of the patent as property and with relation to infringers with which the Patent Office has nothing to do and of which, as at present organized, the commissioner and his assistants have no experience. Now it is the custom of the courts when they propose to amend procedure or practice in the interest of the public to turn to the officers of the court, to the counsel who represent the public, for advice. The Supreme Court of the United States has to-day a committee organized to devise methods of equity practice which shall facilitate the trial of causes, a matter which is peculiarly important to all patent men. That court has appointed sub-committees in all of the nine circuits of the United States and the judges and the bar of all these nine circuits have joined in studying the matter and presenting recommendations. All the bar associations having to do with the federal courts know of the matter and have had ample time to consider and discuss it. The widest publicity has been given to the suggestion before any definite proposal has been made. When the definite proposals are put in their first form they are to go out again to all these committees and to the whole bar for final criticism and suggestion.

The Patent Law Association of Washington, when any matter relating to the patent law is proposed, discusses the reasons *pro* and *con* as far as they may be known, and sends them out to hundreds of interested organizations and individuals, reaching many thousands of interested people, and then collates and digests the hundreds of answers received before endeavoring to reach any conclusion. Such is the obvious, the wise procedure in any matter thus affecting the public.

It has remained for the Commissioner of Patents to follow a different course, and without consultation with the patent bar or the manufacturers or inventors or any part of the public, so far as can be ascertained. He has within the brief time intervening since the Dick Mimeograph case was decided on March 11, 1912, added restrictive and oppressive sections to a previous rough draft of various provisions and has embodied these all in a proposed complex codification of some of the patent law. Closely examined, it appears that this codification has embedded in it some provisions of a special interest to the head of the Patent Office and with it the provisions of compulsory license, etc., which hitherto the Patent Office has publicly agreed are inimical to the patent system. These matters of license, restriction, etc., were, however, considered of the first importance by some of the committeemen in Congress so that we now find them embodied in the bill presented by the chairman of the House Committee, but, in the public press, and under circumstances which suggest inspiration, credited generally to the Commissioner of Patents. The Commissioner of Patents, therefore, appears as the author of this bill, which in the main is taken up with matters with which he has no experience and with which his official duties are not connected in any way. He has, therefore, assumed to endorse provisions of law affecting your property. There never was, in fact, a bill better designed in the interest of the trusts and combinations than this bill. It evidences a lack of knowledge of the principles which govern patent property, but, however that may be, I submit that important property matters of this sort should not receive official endorsement before they have been even presented to the people most vitally interested. If the opinions of the Commissioner of Patents were gaged as they should be with reference solely to the individual opinion of one man without special experience in these lines of work, then that would be a matter of small concern, but unfortunately the impression of many of the Representatives and Senators who frankly confess they have no knowledge of patent law at all (and jokingly say that for that reason they were put upon the patent committees), is that the Patent Office endorses such a proposition because it voices the opinion of those who are well informed in such matters.

I have no merely personal criticism to make. A principle is at stake and it is necessary to illustrate to give point to the objection.

I know that the patent lawyers of the country have been at fault for years in not keeping in closer touch with the trend of public sentiment and with the necessity of meeting a carefully fostered opposition to the patent laws. I know too that you, as inventors and managers of important enterprises, have been at fault in not more closely studying these matters. But the essential and dangerous mistake is in the method of forcing legislation. On the whole, we have fared well with Congress because, however mistaken the occasional reports by committees, students of the patent laws and the patent system have succeeded in preventing such proposals from being

embodied in law, and they have, on the other hand, succeeded in amending the law in some essential points because the men in Congress want to do the right thing. But in the political situation which now exists, the exception is magnified into a rule, and without any careful preliminary study or consultation, measures are proposed which must be passed upon by gentlemen, some of whom have not had an opportunity to read the patent laws and the majority of whom confess to not having studied the patent laws or the patent system. We must protest against thus pushing through important provisions, the majority of which are known even by title to but a small fraction of that part of the public most interested. For the most of these provisions there is no public demand. There is only a carefully cultivated demand backed by some specific interest which is opposed to the general interest.

We are not unmindful of mistakes which have occasionally arisen in the administration of the patent laws, and some of these mistakes we have been carefully studying. We have done more than study them. It is the influence and advice of the patent bar helped by many of you which has done away with many modes of doing business by clients happening to own patents, and laxity in the trial of patent causes. We are to-day engaged in a careful investigation of the whole matter and an attempt to get at what may be done to improve procedure and what is really the complaint of the inventors—that is, of the average inventors. The result so far has been the expression of a practical unanimity of desire to have the equity practice so modified as to reduce the burden of litigation, to have some single court whose final decision shall cover all the circuits, and to have some direct means of reaching the wilful infringer, that is, of securing damages commensurate with the damage done by such infringement.

There is also a practically universal desire that the great mass of information obtained by the Patent Office shall be made available, and that the intricate interference motion practice shall be modified. That the search by the Office shall be more thorough and the rule of infringement in the courts more drastic; that is to say, that there shall be reforms in the court procedure and in the Patent Office procedure. It will be observed that these do not require changes in the fundamental patent laws. No one can study the patent laws without admiration for the completeness with which they cover the theory of the system. We do not say that some amendment from time to time may not be advantageous. Such amendments are now suggested, but unfortunately with nearly fifty proposed bills, many of which it is desired to pass simply for the sake of doing something, it is impossible to get the proper attention for the few constructive propositions we hope to advance. Our time and energy is taken up by meeting the attacks of those who, for want of information, are inimical to the patent system, and especially is this necessary when they are assisted by counsel and advice given without proper reflection or disregard of the consequences involved.

The changes which we have advocated and which I have suggested would of themselves go a long way toward clearing up these matters. Those which have been seized upon and urged as vital are, at their best, productive of minor improvement and, at their worst, are destructive of the patent system.

Two things can be done by patent men, by the inventors and manufacturers—the men interested in the patent system. The real merits of the patent system should be evidenced by hundreds of concrete examples of invention which have created new plants and new industries. We should make the public understand how prices are lowered, wages raised and the drudgery of labor lessened by the work of the scientist and the inventor. There should be then a determined effort to get a specific citation of injury done by means of patents. The mere reference to corporations which own patents and which, happening to own patents, are unfair in their business methods is not in point. All combinations which come within the Sherman Act do so whether they own patents or not. The patents have nothing to do with the matter, as has been decided by the Supreme Court of the United States and recently in the well known Bath-Tub Case.

Make no mistake about the place of invention in our social economy. Nothing is more easily proved than its vitality and force. It is proved not only by all statistics, but by the every-day experience of such men as you and by your advisers, your counsel. We *know* that the influence of patented inventions upon industries is evidenced not only in the production of new inventions, but in the actual creation of new industries within this generation. The electric light, the electric car and motor, electric railways, the telephone, the bicycle, with all its allied features, the gas engine in its varied commercial forms, the typewriter, amateur photograph, cash registers, cash carriers, basic steel, the manufacture of aluminum, the graphophone, the kinetoscope, the half-tone process of photo-engraving, the chrome-tanning process, smokeless powder and other high explosives, acetylene gas, linotype machines, automatic weighing machines, tabulating machines, adding machines, flying machines, and the whole realm of electro-chemistry, all are productions of this generation and all are directly traceable to the impulse given invention by the hopes of reward from the limited monopoly of a patent.

If in some occasional cases there have been attempts to utilize patents to cover more than the contract warranted, on the other hand, in many cases, patents have broken up or prevented commercial monopolies by opening new fields, and the disclosures presented through the patents constitute an almost inexhaustible field of practical value upon which many of these industries have been established after the expiration of the patents, and in many cases, unfortunately, after the inventor or the patentee had failed in receiving his due reward.

This is what the public must know. We must teach it, preach it. To some the arguments—to some the statistics—to some the *argumentum ad hominem* and to some the old-fashioned and still effective

rhetoric. And I may be pardoned for concluding with a specimen of that rhetoric.

No one has better summarized the work of science and invention in the past century than Macaulay:

"It has lengthened life; it has mitigated pain; has extinguished diseases; has increased the fertility of the soil; given new security to the mariner; furnished new arms to the warrior; spanned great rivers and estuaries with bridges of form unknown to our fathers; it has guided the thunderbolt innocuously from heaven to earth; it has lighted up the night with splendor of the day; it has extended the range of human vision; it has multiplied the power of the human muscles; it has accelerated motion; it has annihilated distance; it has facilitated intercourse, correspondence, all friendly offices, all dispatch of business; it has enabled man to descend to the depths of the sea, to soar into the air, to penetrate securely into the noxious recesses of the earth; to traverse the land in cars which whirl along without horses; to cross the ocean in ships which run many knots an hour against the wind. These are but a part of its fruits, and of its first fruits, for it is a philosophy which never rests, which is never perfect. Its law is progress. A point which yesterday was invisible is its goal to-day, and will be its starting point tomorrow."

PATENTS AND CHEMICAL INDUSTRY IN THE UNITED STATES.[1]

By B. Herstein.

Patents are intended to protect intellectual property in the industrial field. The close interrelation between patents and the development of modern industry is a subject receiving sufficient consideration on the part of economists, so that in this place only those features need be dwelt on which characterize the specific relation of patents to the chemical industry and their economic bearing upon this industry in the United States as illustrated in the patent statistics of this country. A chemical patent differs essentially in one respect from all other patents in that the finished product in most instances does not carry any characteristic peculiar to the process used in this manufacture, by which the latter could be identified and by which infringement could be established directly. This is the reason for the many secret and supposedly secret processes prevailing in many chemical establishments here and abroad, a condition which is only partially overcome in this country by the possibility of obtaining patent protection for the product itself if the same be new. Some manufacturers therefore prefer to take the inconvenience and risk resulting from the attempt to keep processes secret, a risk especially great in large establishments with a constantly fluctuating working force, rather than to make them even partially known to the interested public. Nevertheless, it may be said that, taken as a whole, the progress of industrial chemistry in recent years is recorded in the literature (patent) from the patent offices of the world, and that in the number of inventions made and patented the chemical industry is not surpassed if indeed equaled by any other branch of manufacture.

This is true very largely also of the United States. In the careful and instructive study prepared by Story B. Ladd and published by the U. S. Census Bureau under the title "Patents in Relation to Manufacturers" ["Census of Manufacturers," **4**, 776 (1902)] it is stated that up to the time of publication (1902) the following number of U. S. Patents had been issued in the principal branches of chemical manufacture:

Bleaching and dyeing	2,293
Chemicals	2,395
Fertilizers	725
Medicinal compounds	1,746

It will be seen that these patents do not cover all of the numerous branches of the chemical industry. The classification followed by the Patent Office devised to satisfy its special requirements, distributes chemical inventions over a wide range of divisions and subdivisions of which the principal ones can be seen from Table I. This table, which was prepared from the original files of the Patent Office, covers all the chemical inventions protected by U. S. Patents in the lines indicated for the decade 1900–1910, but should not by any means be regarded as including those patents relating to the chemical industry which are classified under other divisions or subdivisions. The table further divides the patents issued during the decade according to the nationality of the patentee and the status of ownership at the time of issue, as far as the records go, showing whether the patents were still the individual property of the applicant or had already been assigned to other interests. The latter may, in some slight measure, be regarded as an indication of the immediate industrial applicability of the inventions, because in the majority of cases it denotes an invention made within an industrial establishment and for this reason possesses more chances of practicability and of being tried out in practice. This feature cannot readily be established in any other way.

The total number of patents issued in the United States between 1900 and 1910 for the classes given in Table I was 4068, of which 3509 fell in Division VI, which embraces chemicals almost exclusively. By far the larger percentage, as is readily seen, covers inventions in organic chemistry, carbon dyes and carbon compounds alone furnishing 1547 patents, or 38 per cent. of the total number. The same percentage of the patents issued, namely 38, and in absolute number 1552, were taken out by Americans, the balance of 2516 patents, or 62 per cent. of all patented inventions enumerated in the table, were obtained by inventors domiciled abroad. Of these 2516 patents, German inventors took out the bulk, namely 1754, or 69.5 per cent., Swiss citizens coming next with 167 inventions, or 6.6 per cent. The following comparison is of interest: The total number of all patents issued in the United States between 1900 and 1910 was 240,000—average per year 30,910—of which those issued to foreigners domiciled abroad

[1] Paper presented at the joint meeting of the Am. Chem. Soc., Am. Electrochemical Soc., and the Soc. of Chem. Ind., New York, April 19, 1912.

TABLE I.—PATENTS RELATING TO PRINCIPAL CHEMICAL MANUFACTURES TAKEN OUT IN THE UNITED STATES DURING 1900-1910, ACCORDING TO NATIONALITY OF PATENTEE AND OWNERSHIP OF PATENTS.

		Totals.		Total, Foreign.	America.		United Kingdom.		France.		Germany.		Switzerland.		Europe, all other.		Foreign, all other.	
		Total patents.	Number assigned.	Total patent.	Total patents.	Number assigned.	Total patents.	Number assigned.	Total patents.	Number assigned.	Total patents.	Number assigned.	Total patents.	Number assigned.	Total patents.	Number assigned.	Total patents.	Number assigned.
	Grand totals	4068	2087	2516	1552	524	212	46	178	29	1754	1324	167	146	162	9	43	9
	DIVISION III.																	
	Class 204; Electrochemistry: Subclasses:																	
18.	Alkalies and chlorine	115	41	45	70	30	13	1	4	..	4	2	2	..	16	6	6	2
59.	Bleaching and disinfecting liquors	30	14	20	10	8	4	1	1	..	12	5	2	..	1	..	..	..
60.	Chlorates	11	4	7	4	1	1	..	2	..	1	1	1	..	..	..	2	2
51.	Dyes and pigments	22	13	3	19	11	..	..	..	..	..	..	2	2	..	..	1	..
62.	Carbides	73	42	14	58	39	3	..	2	..	3	1	..	..	4	..	2	2
27.	Tanning	5	3	..	5	3	3	..	..	..	..	..	..	..	..	..	..	..
	Total	256	117	89	167	92	21	2	9	.	20	9	7	2	21	6	11	6
	DIVISION VI.																	
	Class 8; Bleaching and dyeing: Subclasses:																	
1.	Carbon dyes	862	819	843	19	9	11	5	11	4	701	685	115	113	5	3	..	..
2.	Bleaching	50	16	30	20	5	8	.	3	..	17	11	..	..	2	..	..	..
5.	Dyeing processes	141	70	110	31	10	8	1	9	3	79	56	..	..	14	..	..	..
6.	Dyes	38	15	16	22	5	3	..	3	1	10	9	..	..	..	..	..	..
20.	Mercerizing	53	7	29	24	4	11	1	3	1	10	1	..	..	5	..	..	..
13.	Mordants	43	12	21	22	5	2	1	3	..	13	6	..	..	3	..	..	..
	Total	1187	939	1049	138	38	43	8	32	9	830	768	115	113	29	3	..	..
	Class 23; Chemicals: Subclasses:																	
1.	Acids, mineral	215	77	99	116	41	8	3	6	..	62	32	1	1	21	..	1	..
5.	Fire-extinguishing compounds	13	5	8	5	1	1	..	1	..	4	4	..	..	1	..	1	..
	Catalytic bodies	17	9	12	5	2	..	..	1	..	10	7	..	..	1	..	..	..
10.	Metalloids	86	29	31	55	23	5	..	9	1	14	5	..	..	2	..	1	..
11.	Packing chemicals	14	6	4	10	5	1	..	1	..	2	1	..	..	..	..	..	..
3.	Apparatus	61	11	21	40	10	7	1	..	..	10	..	..	..	3	..	1	..
13.	Salines	337	118	191	146	51	43	15	16	2	98	50	3	..	21	..	10	..
21.	Ammonia	47	13	41	6	1	1	5	1	..	27	7	..	..	4	..	1	..
22.	Soda and potash	42	12	18	24	7	1	..	3	..	9	5	1	..	3	..	1	..
24.	Carbon compounds	685	448	555	130	51	18	3	38	10	450	359	32	25	16	..	1	..
	Total	1517	728	980	537	192	92	27	76	13	686	470	37	26	72	..	17	..
	Class 52; Explosives: Subclass:																	
3.	Nitro compounds	156	61	59	97	55	14	1	8	..	28	5	..	..	8	..	1	..
	Class 167; Medicines: Subclasses:																	
5.	Hair dyes and tonics	20	2	4	16	1	.	..	..	..	2	1	..	..	..	.	2	..
4.	Extracts	82	16	38	44	6	8	2	4	.	18	6	..	..	6	..	2	2
7.	Internal remedies	89	41	66	23	6	2	..	4	2	52	31	2	1	3	..	3	1
9.	Topical remedies	71	19	26	45	10	2	..	..	..	20	9	1	..	3	..	..	..
6.	Insecticides	81	9	12	69	8	2	..	..	..	6	..	1	1	1	..	2	..
3.	Disinfectants	306	68	66	240	57	10	.	25	2	19	9	..	..	7	..	5	..
	Total	649	155	212	437	88	24	2	33	4	117	56	4	2	20	..	14	3
	DIVISION XV.																	
	Class 106; Plastic Compositions: Subclasses:																	
37.	Pyroxylins	43	10	23	20	4	2	1	9	1	10	3	2	1	.	.	..	..
40.	Viscose and cellulose	59	25	42	17	9	5	4	4	2	28	9	1	1	4	..	..	..
	Total	102	35	65	37	13	7	5	13	3	38	12	3	2	4	..	..	..
	Class 18; Plastics: Subclass:																	
51.	Pyroxylin	14	10	2	12	9	1	.	..	..	..	..	1	1	..	..	..	..
	DIVISION XXXI.																	
	Class 87; Oils, Fats and Glue: Subclass:																	
7.	Glue	23	6	11	12	5	1	..	1	..	8	1	..	..	1	..	..	..
	Class 134; Liquid coating compositions: Subclasses:																	
72.	Treating lead salts	4	..	2	2	..	2	.	..	..	..	..	..	..	..	..	..	..
54.	Paint rubber	9	1	2	7	.	.	.	.	..	1	1	..	..	1	..	..	..
17.	Rubber	6	3	2	4	2	.	.	.	.	1	..	..	..	1	.	..	..
59.	Iron salts	13	1	2	11	1	.	.	1	.	1	..	..	..	..	..	..	..
60.	Lampblack	16	2	8	8	2	.	.	1	.	7	..	..	..	..	..	..	..
67.	Lead salts	18	7	4	14	7	2	.	.	..	1	..	..	..	..	..	..	..
77.	Ultramarine	2	.	2	..	..	.	.	2	..	..	..	..	..	..	..	..	..
78.	Zinc salts	39	7	12	27	6	4	1	1	..	5	..	..	..	2	..	..	..
79.	Pyroxylin	14	4	7	7	3	.	.	1	..	4	1	..	..	2	..	..	..
	Total	121	25	41	80	21	8	1	6	..	20	3	..	..	7	..	.	.
	Class 203; Ammonia, water and wood distillation: Subclasses																	
1.	Ammonia, including turpentine	13	2	6	7	2	1	.	.	..	5	..	..	..	.	.	.	.
4.	Turpentine processes	17	6	2	15	6	1	..	..	..	2	..	..	..	.	.	.	.
3.	Turpentine apparatus	13	3	..	13	3	.	..	..	..	.	..	..	..	.	.	.	.
	Total	43	11	8	35	11	1	..	.	..	7	..	.	..			..	..

were 38,930 in number, average per year 3,540, or 11.4 per cent. In the chemical industry, according to Table I, the percentage of patents issued for inventions made and to patentees domiciled abroad was more than five times as great, namely 62 per cent.

Table II gives the average number of patents issued in the United States yearly during 1900 and 1910, average number and percentage quota of patents relating to chemicals only, granted according to nationality and domicile of patentees. Patentees of foreign birth residing in the United States, whether or not citizens of this country, are included among American patentees.

TABLE II. AVERAGE NUMBER OF TOTAL AND CHEMICAL PATENTS ISSUED TO FOREIGNERS DURING 1900–1910.

To citizens of	Average number of all patents issued between 1900 and 1910.	Average number of chemical patents.	Percentage of chemical patents issued to citizens of
United States	27,375	155	0.5
Germany	1,043	175	16.8
Great Britain	900	21	2.3
France	323	18	5.7
Switzerland	87	17	2.0

The low percentage of chemical patents taken out by citizens of the United States is of course due to the great number of patents granted to American citizens in other industries and as such would be without any special significance, were it not for the fact that the absolute number of chemical patents taken out by citizens of the United States in their own country is considerably smaller than the number of patents issued in the U. S. to foreigners collectively and even smaller than the number of patents issued in the U. S. to Germans only. This preponderance of inventors residing abroad, especially German, in the chemical industry, applying for United States patents, has been pointed out already in the Census study referred to above (*Loc. cit.*, p. 759), the result being as follows:

During the decade of 1890–1900 there were granted in the United States 622 patents for "Carbon Dyes" and 312 patents for "Carbon Compounds," other than dyes. Of these, 609, or 97.9 per cent., and 281, or 90 per cent., respectively, were issued to foreigners abroad, principally Germans. Table III, summarizing the salient features of Table I, shows that during the decade following this proportion had changed very little, if at all.

TABLE III.—SUMMARY OF CHEMICAL PATENTS ISSUED IN THE U. S. BETWEEN 1900 AND 1910, BY CHARACTER OF PATENT AND DOMICILE OF PATENTEE.

	All patents.		Patents for carbon compounds and bleaching and dyeing processes.		All other patents.	
	Issued.	Assigned.	Issued.	Assigned.	Issued.	Assigned.
Total	4068	2087	1738	1353	2330	734
American	1552	524	200	75	1352	449
German	1754	1324	1247	1111	507	213
Foreign, all other	762	239	291	167	471	72

This table shows that the total number of patents issued during the period under consideration, *i. e.*, 4068, only 1552, or 38 per cent., were taken out by resident Americans. Germans residing in Germany obtained 1754 patents, or over 43 per cent., and 762 patents, or little less than 19 per cent., were issued to other foreigners residing abroad. In the groups, "Carbon Compounds, Bleaching and Dyeing Processes," 1738 patents were issued, of which only 200, or 11.5 per cent., were applied for by American citizens. This apparently indicates a slight progress against the preceding decade; yet such a condition must be admitted to be far from satisfactory considered from any point of view and least satisfactory when the material loss arising from such a situation is computed, since the groups mentioned constitute probably the most profitable branches of the chemical industry.

The statement has been made therefore that the fact that a patent was assigned prior to its issue is to some degree a measure of its immediate industrial utilization, and this is, for obvious reasons, even more true in the case of foreign applicants. The number of patent assignments given in Table I specifically for each country, and in a summary way in Table III, is therefore of some significance. Expressed in percentage for the whole of the field covered by this table they are as follows:

Assignee residing in:	Percentage of U. S. chemical patents assigned before issue.
United States	38.8
	Per cent.
United Kingdom	21.2
France	16.3
Germany	75.5
Switzerland	87.4

Patents issued to Swiss citizens cover almost exclusively Carbon Dyes and other carbon compounds, both industries being highly developed in that country and carried on by large corporations almost exclusively in the district of Basle. The proximity to Germany and a patent legislation—since changed—which permitted the infringement of foreign patents, are largely responsible for the growth of these manufacturers in Switzerland.

Table III gives the number of all patents issued to Germans living in Germany during the period covered at 1754, of which 1324, or 75.5%, were assigned before issue. The highest ratio of these assignments is reached in inventions relating to Carbon Dyes, namely 685 out of 801, or about 98 per cent. One additional point as brought out in this table deserves emphasis. Of the 1754 patents issued for German inventions, 1247, or a little over 71 per cent., related to carbon Dyes and compounds and bleaching and dyeing processes, in all only 5 subdivisions out of more than 40 accounted for in Table I. The number of the assigned inventions was 1111 out of 1247, or practically 90 per cent., and of these, as is shown in Table IV, 844 inventions, or 68 per cent., were assigned to only four companies, who in connection with one other company by an interchange of stock and division of profits under an agreement to last 50 years from 1904, work on a "community of interest" plan, as revealed by their own reports. (H.

Schultze, *Entwicklung der chem. Industrie, Halle*, 1908, p. 786.)

TABLE IV.—AMERICAN PATENTS ASSIGNED TO SPECIFIC GERMAN COMPANIES, BETWEEN 1900 AND 1910.

Name of company.	Carbon compounds.	Bleaching and dyeing processes.	Carbon Dyes.	Total.
Aktiengesellschaft für Farben, Berlin	9	1	48	58
Badische Anilin Fabrik	34	34	188	256
Bayer & Co., Farbenfabrik, Elberfeld	104	19	217	340
Meister Lucius & Bruening	58	17	115	190
Total	205	71	568	844
Total patents issued to Germans	450	96	701	1247

A patent is essentially a monopoly, maintained with the consent and enforced with the help of the government. Its prime object and recognized social value consists in promoting the material development of industry in the country of issue. Viewed from this point, it seems that the development of the chemical industry in the United States has not kept pace with the number of patents issued. Our patent laws are stringent as to novelty and lenient to the inventor or his assignees. These practically certify the first and give far-reaching protection to the latter—much more protection than in any other country—because the American law recognizes the patentability of the product as such, so that no other process or improvement thereof can touch it during the life of the patent in the United States except with the consent of the original inventor or his assignees.

This feature permitting a product patent and specific only of the American patent law presents a serious problem especially in its relation to the chemical industry. In this industry the product is of paramount importance. The process by which a given product is obtained is not absolutely characteristic thereof, because the same product may be obtained in different ways, varying only little or none at all in the degree of commercial feasibility. But it is self-evident that under the American law the owner of a product patent can prevent the manufacturer of this product by others, even if their process were entirely new and not merely an improvement on the original process, and though this new process were preferable materially, or otherwise offered inducements for its adoption. In the end, such a policy works against industrial progress or against the basic purpose of all patent legislation.

The liberal intention of the law to give the original inventor as much opportunity as possible to derive material benefit from his invention may be considered commendable if the interests of the inventor were the sole factor to be looked after. This, however, is not the case. A patent is a contract between the patentee and society-at-large, a *quid pro quo*, in which the interests of the state are entitled to at least equal consideration with those of the inventor. It is a debatable question whether these interests are sufficiently protected where an individual, single or corporate, possesses legal power to prevent the utilization of improved manufacturing processes as applied to specific products covered by patents.

In the earlier times of our industrial development, such a provision of law may have had its justification. Inventions were then largely due to the efforts of single individuals working along certain lines with little fear of interference. The inventions wanted in complexity, their value could be more easily appreciated, the utilization was more immediate, the result more direct. The progress of science and the interdependence of its several branches have changed these conditions entirely. Only in rare instances can one single man overlook the entire field of work in which he is engaged. The personal element, previously so large a factor, has gradually been eliminated to a great extent and the noteworthy achievements of to-day in science, and in industry as well, are the results of many brains focused upon the same object, sometimes working together, often working independently, but always influencing one another. It is the collective product of the mass and not the individual product of the unit. In no branch of industrial and scientific activity perhaps is this principle of coöperation better illustrated than in chemistry and nowhere has it been accompanied by more beneficent results for society-at-large. The industrial and scientific progress of chemistry is to-day carried on in huge establishments by any army of workers each contributing his share towards the whole. This results daily in the discovery of many new products, some of immediate, others of potential commercial value, and for this reason the practice of protecting all new discoveries by patents has become universal. But in most industrial countries, the patent protects the process only and for their own protection the inventor and his assignees are therefore compelled to experiment in all possible directions that may conceivably lead to the same product in order to insure for themselves the reward coming from its manufacture. If, on the other hand, the material reward arising from a certain specific chemical manufacture be sufficiently large, competitors will be drawn to it and these will bend their energies toward devising new processes in order to be able to take up this manufacture without infringing upon existing patents. The result is doubly beneficent, not only because it stimulates legitimate rivalry, but more so perhaps because work along such lines is bound to lead to discoveries often entirely unforeseen and pre-eminently useful. But where the patent covers the *product*, irrespective of the *process* for its manufacture as in the U. S., the tendency will be, for obvious reasons, toward stagnation. This feature is borne out statistically, though, of course, only in a very inconclusive way, for want of adequate data, as follows:

Table IV shows that the four German companies there mentioned had secured on an average about 80 patents per year in the United States. These same four companies have taken out in 1907, which if anything was rather an off-year in Germany, 181 patents. (James Baron, "Chemical Industries on the Continent," 1909).

There is yet another important feature to the U. S. patent laws, not found in most other industrial countries, which in the opinion of competent observers is not calculated to promote industry and by which the chemical industries especially, owing to their peculiar nature, are negatively affected.

Contrary to the requirements of the patent laws of most other industrial countries, the Unites States does not specify compulsory working of the patent issued, but permits the patentee, and him only, to import his products into the United States from whatever place he chooses, giving him a monopoly of the market without imposing upon him any obligation or demanding of him any equivalent except the minimum fee paid originally to the Patent Office. In the case of the American inventor such a situation will develop only under exceptional circumstances; with the foreigner, however, it is for obvious reasons the rule, in the chemical industry especially. The American market is the most valuable in the world and the foreign inventor or his foreign assignees naturally take all the advantage that the law gives them to exploit this market as profitably as they can. This very largely accounts for the tardiness with which the chemical industry develops in the United States, especially in those branches which depend preponderatingly upon inventions and therefore cannot be gaged by any tariff legislation under the theory of cost equalization or under any other theory.

Up to 1907 the English patent laws did not require compulsory working in England of patents issued there, but the situation became so unbearable that the law was changed and the compulsory working feature established with the result that, according to a report in the *London Times* (March 23, 1911) up to 1911 50 foreign firms had begun, or were about to begin, manufacturing in England, involving an investment of about $4,000,000 and the employment of nearly 7,000 wage earners, with a weekly pay roll of $40,000. This did not include the large number of licenses granted by the patentees to English manufacturers under the best conditions obtainable, choosing this alternative rather than suffer the threatened repeal of the patent. German and American interests were particularly affected by this change in the law and the manufactures introduced were those of filaments for electric lamps, photographic films especially for the cinematograph, anilin dyes, medicines, glazes, oxygen, etc., all practically chemical manufactures, besides processes for making mercerized cotton, and food products (which are related chemical industries).

With reference to France, it has been stated on good authority that many firms engaged in the chemical industry in that country are controlled by foreigners, and this also is largely due to the compulsory working feature of the French patent laws. Germany imposes the same obligation, though it is waived in favor of American patentees. In the United States, practically single in this respect among the industrial nations of the world, the progress of the chemical industry as reflected by the patents issued must be traced not by the broadening of the domestic production but in the imports only.

What has been said above is to be considered as an attempt to point out anew those fundamental characteristics of our patent legislation which, in their bearing upon the chemical industry at least, are calculated to retard rather than to promote the development of manufactures in the United States. It must be recognized that chemical manufactures are but a small, even if a very important part of our industrial structure. Expressed in the number of patents taken out, the figures quoted before show that scarcely more than one per cent. of patents issued cover inventions properly called chemical. Thus, even if admitting that this small percentage is in a large measure the result of a retarded development and should therefore the readier call for corrective, it is obvious that from the viewpoint of national economy no legislative remedial measures may be expected unless it can be demonstrated that the interests affected adversely are considerably greater than indicated, or that correction can be applied without prejudice to the many other complex questions involved.

As American chemists, however, working in the United States, and virtually affected by the status of the chemical industry here, we are preëminently interested, and it is our duty to see that the proper conditions for the natural development of our industry be maintained and all barriers affecting it negatively be removed. No one at all acquainted with the subject will deny, and a study of the foreign trade statistics will immediately show, that the building up of the chemical industry in this country has been extremely one-sided. The manufacture of heavy chemicals, on the one hand, is in most respects on an equality with the best anywhere, and the same is true of the staple organic and medicinal chemicals. The manufacture of so-called fine chemicals, however, and especially of coal tar and coal tar products, is sorely inadequate, retarded or even dwarfed if you will. And this is not for want of raw materials or other primary elements essential for the existence of such manufactures, but more so because both tariff and patent legislation have created a situation forcing enterprise in one direction and preventing it becoming engaged in the other. Unlike the heavy chemical industry, the manufacture of fine chemicals and of coal tar products derives its profitableness exclusively from patents. The greatest material gain comes during the life of the patent, owing to the monopolistic character of the latter, and naturally the profit is not lessened or otherwise interfered with however high the duty may be put, so long as domestic production is made impossible and imports are permitted, as is the case in the U. S. Here, if anywhere, the consumer pays the full duty. After the patent has expired the specific product may have gone largely or entirely out of use, or the owner of the patent will have gained so much experience that he can lessen very materially the cost of production and consequently also the selling price without affecting much the rate of profit, or he will have developed

some new manufactures along the same line, obtain patent protection for them and the profit from these will be sufficient to compensate him for the diminished sales and profits on the original product. Competitors who take up the manufacture of articles, patents on which are about to expire, expect to live, so to speak, on the gleanings left on the field after a rich harvest. In the United States, with reference to chemical manufactures especially, the government is expected to equalize by tariff legislation conditions which have become unequal in time and the economic handicap cannot, therefore, be eliminated without putting serious burdens directly or indirectly on the consumer.

That industries can be legitimately and should be deliberately promoted by judicious tariff legislation is not open to much controversy in this country, but tariff legislation is but one out of the many factors influencing our enormously complex industrial life, and as far at least as chemical manufactures are concerned, judicious patent legislation is undoubtedly of equal importance with the former. It was the purpose of this paper to point out and to emphasize this importance, and the extent to which this has been accomplished will express the degree of justification for its having been presented before this society.

THE ABUSES OF OUR PATENT SYSTEM.[1]

By L. H. Baekeland.
Received April 10, 1912.

A recent decision of the Supreme Court (Sidney Henry, *et. al.*, *vs.* A. B. Dick Co., March 11, 1912. No. 20, October Term, 1911) upholding the right of patentees to dictate under what conditions a patented article shall be sold, or shall be licensed, has become the object of much criticism. One of our newspapers repeats the comment, that this decision could be interpreted to its extreme limits so as to mean that "it would enable the patentee of a window frame to dictate that all the material of a house in which the frame was to be used must be procured by him." But that argument overlooks the fact that nobody is compelled to buy that particular patented window and that the public-at-large can purchase any other window frame not patented, or of which the possession is not submitted to any restrictions. The Supreme Court decision simply means that the owner of a patent, in selling or licensing under it, has the same privileges that the owner of any other private property has. For instance, the proprietor of a lot can sell it with the restriction that if any house is to be built on it, the materials for this building shall be purchased from him. It all depends whether the purchaser is willing to submit to these terms or prefers to forego acquisition under such restrictions. To assail this decision of the Supreme Court, is to deny the elementary rights of private property, or to deny that a patent is private property.

Justice Lurton, in expressing the majority opinion of the Supreme Court, very correctly says: "When the patent expires, the public will be free to use the invention without compensation or restriction."

Outside of this limitation, why should restrictions be put upon ownership of patents, which do not exist for other forms of private property? An invention is the creation of something which did not exist before. Is the creator of this invention not entitled to undisturbed ownership, at least for a short period of 17 years, when the ownership of real estate, or other private property is undisturbed and continues forever?

And yet, real estate always existed long before it got in the hands of private owners. Its mere possession does not imply any special merit, nor does the private ownership of real estate confer any benefit upon the community. Nevertheless, real estate can be left idle at the whim of the owner, who in the meantime benefits by the enhanced value, the unearned increment, conferred upon his property through the enterprise of the community at large, and more especially by the enterprise of his immediate neighbors, who take the trouble and the risk to develop their own real estate, while he just remains inactive.

So that, in this and many other ways, the owner of real estate, or other private property, has an incomparably greater scope of unquestioned property rights than a patentee. Furthermore, these rights do not cease after 17 years, but continue forever.

It is a significant fact that in many cases, the persons who object most to patent rights are just those who have lived in surroundings where industrial or intellectual development is least apparent.

In some parts of the country, the word "patent" is scarcely known, and the conception of a higher class of property than that which is merely acquired by inheritance or money purchase is difficult to understand. On the other hand, the conception of intellectual property rights is one of the symptoms of a higher state of civilization.

I may point out on this occasion that the little state of Connecticut takes out more patents than all the Southern states together.

Most people imagine that patent laws are for the exclusive benefit of inventors, and this regrettable mistake leads to many misunderstandings. Were this opinion correct, patent laws would mean class legislation, and would be as unfair, as undemocratic, as unwholesome, and as dangerous as any other class legislation.

But the patent laws, as framed under the Constitution of the United States, are primarily conceived for the benefit of the nation. No country has benefited more by its patent system than the United States. Compare the tremendous industrial development of such nations which have liberal patent laws, like the United States, Germany and England, with that of the Latin countries, where patent laws are less favorable to the inventor.

There is one civilized country, Holland, which until recently had no patent law whatever, and allowed the unrestricted use of any invention. This ought to have been the Paradise of Infringers; it was easy enough to use freely in Holland processes patented in other countries, and to distribute from there, infringing goods to all the countries of the world. Yet what

[1] Paper presented at the joint meeting of the Am. Chem. Soc., Am. Electrochem. Soc., and the Soc. of Chem. Ind., New York, April 19, 1912.

was the result? Holland, with her highly developed commerce, her abundant money supply, with a race of intelligent and enterprising men, remained industrially undeveloped, and still ranks as one of the least industrial among the countries of the world. Why? Because there was no incentive to saddle oneself with all the risks and outlays of starting a new enterprise or of improving methods for manufacture, knowing beforehand, that in case of success, one's neighbor could simply do the same thing without any restriction whatsoever.

The fact that good patent legislation is for the benefit of the whole nation is too often lost sight of, and it behooves every good citizen of this country to help improve our patent laws and the administration thereof. A patent is simply a contract between the nation and an individual, the inventor. By that contract the inventor discloses to the community-at-large the results of his intellectual work; by doing so, he enables others to get acquainted with his work, and to improve thereon, and this stimulates further research, invention and enterprise. You will find that newly disclosed patents are usually followed in rapid succession by several improvements thereon, conceived by others, but patterned on the original invention. The inventor, in disclosing his secrets, confers a benefit on the nation, and the nation, in return, gives him for a rather short number of years the sole use of his invention—followed immediately afterwards by absolute confiscation in favor of the public. The period of this limited monopoly is none too long if we take into consideration the time it takes to develop an invention into commercial shape; in many cases, inventions reach the money-earning stage only after the patents on which they are based have expired. In the meantime, the disclosures made by the inventor stimulate enterprise and further invention, and induce the ideal form of competition by improvement most advantageous for the consumer —competition by improvement. So that, practically, the granting of a patent is simply a business contract between two interested parties: the nation and the inventor.

Up to this point everything goes well enough. Our patent laws, although not perfect, are generally considered as a model of good patent legislation; they were conceived in a broad and fair spirit, and the best answer to those who find too much fault with them is, that in all foreign countries, including Germany, whenever a modification has been made in their patent laws, the change has always brought them a step nearer to the American patent system.

The real trouble begins when this business contract between the nation and the inventor has to be enforced. It is there that the patentee does not get "a square deal." After the inventor has faithfully performed his part of the contract, and has disclosed his invention to the nation, the nation hands him a "gold brick."

Woe, indeed, to the poor inventor who tries to enforce his rights against wealthy infringers, aided by skilful lawyers. His well engraved United States patent parchment may then become his certificate of entrance to the poor house, or to the lunatic asylum. All this tends to discourage invention by independent individuals and paralyzes the stimulation of invention our Constitution intended to promote by the patent law.

In other words, although the patent law of the United States is about as fine a piece of good progressive legislation as was ever conceived, its enforcement in the United States courts is subject to so many uncertainties, complications, delays, and to such horrible expenses, that the man with limited resources is at an inexpressible disadvantage.

If any one asks my advice, whether he should take out a patent or not, my invariable answer is: "Can you find the money to defend your right in court? If not, do not waste any time or money on a patent."

Here, then, is an instance of a beneficent and well planned law, meant to be fair to everybody, and which through absurd rules of practice and procedure, as sanctioned by American courts, has entirely deviated from its purposes. Meant to stimulate research and industrial development, it has merely become a pretext of playing bluff against bluff, trick against trick, by skilful acrobats of the profession of law.

As our patent law is used now, it is certainly a Godsend for large corporations, lawyers and experts.

About three years ago, one of the most successful law practitioners, a candid man, declared publicly before the N. Y. Section of the American Chemical Society [THIS JOURNAL, 1, 201 (1909)] that as he was about to retire from business he had no further hesitation in stating that in the many patent cases he had won for his clients, the latter seldom, if ever, got any settlements for damages, and if they did, it was a mere fraction of the fees he had collected from them for defending their case; he took the occasion to ridicule the absurd conditions prevailing in our courts, which make this possible. Some experts reap just as golden a harvest by this state of affairs. Not so long ago I overheard a chemist, whose specialty is to testify in patent cases, discussing with an opposing expert a patent case in which he was retained; his conversation was boisterous enough that any one present could hear it: "This is the most interesting patent we ever had in that line," he said. "Do you realize the fact that this means for you and me at least five thousand dollars a year for at least five years and....", he significantly added, "this will give us an opportunity to learn much organic chemistry?"

This, indeed, is the way some experts get their knowledge of chemistry: their clients pay for their tuition.

As for wealthy corporations, it has become obvious that the skilful handling of patent cases places them at an untold advantage against their smaller competitors. For them, a well organized patent department is a reliable machine, where money is the lubricant. This machine, in its slow-but-sure grinding way, can reduce to pulp any of the smaller competitors. For large corporations, the maintenance of such a machine

with a staff of lawyers and experts, is merely a small side expense. By its aid, they can bluff their weaker competitors into quick submission. If this is not successful, they can drag out a patent suit indefinitely, until the weaker opponent, unable to bear the ever-increasing expenses, collapses and withdraws.

These tactics are well known and have been played successfully, whether it was to uphold a worthless patent, or to obtain immunity in case of infringement. In every case, the wealthy corporation is sure of the outcome of the game and plays "Heads I win, tails you lose."

Although these facts are sufficiently known by all who have practical acquaintance with patent litigation, the public-at-large is ignorant thereof, and cheerfully imagines that the inventor has a sure thing and that everything comes his way. We hear fairy tales of the fabulous wealth of inventors. I know many inventors, and very, very few of them ever obtained any important sum of money by their inventions, as such. If some have become rich, it was as manufacturers or as business men, and not merely by selling inventions. Most patents sold as such, do not even repay the expenses involved in the preliminary work connected with them.

As matters stand now, the public does not get the benefit of our patent laws; and the law thus misses its highest purpose. Our degenerated rules of practice and procedure simply serve to strengthen the rich and mighty, who apparently disburse the funds for litigation, but in the end make the consumer, the public, pay the bill. But the consumer does not know this, and in his cheerful ignorance believes, in the meantime, that he has nothing to do with patent laws and patent litigation, so the matter does not interest him. On the other hand, many public-spirited lawyers, disregarding narrow-minded professional interests, have spared no pains to expose this condition of affairs and have urged reforms.

Why, then, should this state of affairs have persisted so long? Why should our otherwise excellent patent laws have become so perverted in their applications? Simply again through the sheer indifference of the directly interested parties—the public and the inventor.

As to the inventor, he is most to blame. I have met few inventors who, when asked for a remedy, did not come out right away with impractical or far-fetched cures. Most of them want to make a radical change in every department of our patent system, forgetting that it is easier to break down than to build up. Others suggest pet remedies of their own, but the worst of all is that no two inventors can agree on the subject. In justice to the inventors, I should mention that most of the lawyers I have met are in the same predicament. In the meantime, the real fact is that very few reforms are necessary in order to remove the absurd conditions of our patent system, and these reforms can easily be accomplished if we can only agree on them. This I shall try to explain:

Formerly, all patent cases, on appeal, went by right, from the lower courts to the Supreme Court of the United States. The latter court not only rendered final decisions, but, what is more important, saw to it that the proper rules of practice and procedure were observed in the lower courts. The Supreme Court acted practically as a supervising body on our patent system, and lent considerable prestige to it, but through the rapidly increasing development of this country, the cases before the Supreme Court became so numerous that finally it took three to four years, after an appeal was filed, before a case could be heard. This amounted practically to a denial of justice, because some of the patents expired before their case was reached.

So, in 1891, a remedy was inflicted which has proved to be much worse than the ailment. Nine Circuit Courts of Appeal were organized, and each court, independently, can give *final* decision in patent cases. This has brought us into an intolerable condition of affairs. Indeed, each Circuit Court of Appeals can adjudicate only for its own circuit, and being independent of control by any other Circuit Court of Appeals, each court makes decisions as it thinks right, based upon the evidence submitted and in accordance with its own view of the law. So that we have now the absurd condition that some patents are valid in some parts of the country and invalid in others. Any litigant with much money, who has been beaten in one circuit can carry on his infringements with impunity in an adjacent circuit or drag on new suits forever and a day. While doing so, he knows very well that he can postpone a final decision as long as he is willing to pay his lawyers. But this is not the worst of the situation. Since the Supreme Court of the United States is no longer *by right* the final arbitrator in case of appeal, our whole patent system has lost the prestige and correcting influence of a final court, that supervises the faithful observance of proper rules of practice and procedure.

I am told that we have some good rules of practice, formulated long ago by the Supreme Court, but that since the practical elimination of this court in patent cases, lawyers and experts, for reasons of their own, have acquired the habit of disregarding these rules or "waiving them by courtesy" for reasons of their own. I am even told that if these rules were honestly adhered to, the testimony of any patent suit could be ready for the court at the end of six months.

A bill for a court of Patent Appeals has been pending now before Congress from year to year, and seems to meet with almost unanimous approval, even from lawyers. The only serious opposition seems to be on the part of some politicians, who do not like the idea of new judgeships being created while their political opponents are in power. If this argument is kept up, the bill will never pass, unless we unite our voices to demand it.

Give us a Court of Patent Appeals which will render final decisions by which we can abide, instead of the absurd condition of affairs where one Circuit Court of Appeals can oppose its decision to that of another. Give us a Court of Patent Appeals which shall formulate and maintain common-sense rules of practice

and procedure, and stop the abominable custom of taking unrestricted testimony without a presiding judge. Let us exclude all testimony which has nothing to do with the case, but which is entered as a trick to prolong litigation indefinitely; as a pretext to pad the records, as a technical dodge to drag on the case, and to defer judgment; as a means of saddling your poorer opponent with ever-increasing expenses until he staggers under the load and is ready to give up the fight, if in the meantime the term for which the patent has been granted has not expired.[1]

Let testimony be taken in open court as it is done in Germany, in England, and by other nations, where cases are tried and settled at relatively small expense and in a short time, instead of taking many, many years, as happens here. In Germany and in England, patent infringements are treated just like any other violation of property rights; with the same severity as though somebody had stolen or damaged another man's property.

While we are about it, let me mention the urgent need of a new patent office building. That awkward Greek temple in F street was acceptable enough when our country was so much smaller. It now has become a conjested, cumbersome, impractical fire-trap in in which, some day, all the valuable records of pending and allowed patent cases will be destroyed. Whenever this occurs, and it may happen to-morrow, it will prove a real calamity for those of our manufacturers whose business is dependent on patents. That fire will give unusually unfair opportunties of making money to those who live and thrive on patent litigation.

The patentees of the United States have paid, up to date, to Uncle Sam, about seven million dollars in excess over expense of the Patent Office. This fund has now accumulated to the credit of the Patent Office. Why should it not be used to construct a well-equipped modern business building, where our patent records, which you and I have paid for, are kept in fireproof rooms? Such a building should be provided with all the equipment necessary for a thorough search. Many important literature references are not available in the Patent Office. It seems incredible, but complete copies of patents issued in some countries like Belgium, France and Canada are lacking. If these lacking records had been available to the Examiners, many invalid patents would not have been issued through sheer want of means of obtaining full information as to prior published disclosures. It is truly astonishing that under such handicaps, our overworked patent examiners have been able to furnish so much good work. An up-to-date patent building should possess also a complete laboratory, where simple chemical and physical questions can be demonstrated promptly and easily.

A very desirable reform in the practice of the Patent Office would be the introduction of the German system of public objection to an "allowed" patent, before it is definitely "issued." In Germany, in Austria, and in England, after a patent has been examined and allowed by the Examiner, the title and the claims are published and copies of the text can be obtained from the Patent Office. Then, during a period of two or three months, objections to the issue of the patent can be filed in writing by anybody. Copy of the filed objections are forwarded to the applicant, who then has a few months to file an answer. In this way, the examiner has the benefit of a thorough public discussion of the subject before that patent is definitely issued. This involves a delay of several months in the issue of a valid patent, but this is a very small hardship, indeed, if one takes into consideration the fact that a patent issued after severe public contestation gains much in value by its record. Furthermore, this procedure is now successfully used in the U. S. Patent Office for the registration of trade-marks.

Some other useful reforms have been suggested, reducing the needlessly large number of appeals in case of interference.

Our interference rules may appear very logical in accordance with the conception that in the United States, a patent belongs to the first diligent inventor, independently whether he be the first patent applicant or not, as long as his invention has not been in commercial use before that period. To the uninitiated, this may seem an excellent safeguard to insure that the first inventor should receive the reward of his intellectual work. Unfortunately, any poor inventor, who has been through interference cases, knows that without much money, an interference case becomes almost a hopeless proposition if he has to deal with

[1] Judge Hough, in giving his opinion in the famous Seldon case, where 36 huge volumes of printed testimony were submitted, took occasion to denounce our absurd methods of patent litigation, as follows:

"It is a duty not to let pass this opportunity of protesting against the methods of taking and printing testimony in equity, current in this circuit (and probably others), excused if not justified by the rules of the Supreme Court, especially to be found in patent cases, and flagrantly exemplified in this litigation. As long as the bar prefers to adduce evidence by written deposition, rather than *viva voce*, before an authoritative judicial officer, I fear antiquated rules will remain unchanged and expensive prolixity remain the best known characteristic of equity.

"*But reforms sometimes begin with the contemplation of horrible examples*, and it is, therefore, noted that the records in these cases, as printed, bound and submitted, comprise 36 large octavo volumes, of which more than one-half contain only repeated matter—*i. e.*, identical depositions with changed captions and exhibits offered in more than one case. In reading the testimony of one side in one set of cases there were counted over 100 printed pages recording squabbles (not unaccompanied with apparent personal rancor) concerning adjournments—and after arriving at this number it seemed unnecessary to count further. In many parts of the record there are not five consecutive pages of testimony to be found without encountering objections stated at outrageous length, which may serve to annoy and disconcert the witness, but are not of enough vitality to merit discussion in 2000 pages of briefs. Naturally tempers give way under such ill-arranged procedure, and this record contains language, uncalled for and unjustifiable, from the retort discourteous to the lie direct. All this lumbers up the court room, *while clients pay for it.*

"Even when the evidence in equity was taken up by written answers to carefully drawn interrogatories, the practice was not marked by economy or celerity; but stenography and typewriting, the phonograph and linotype, have become common since our rules were framed, have made compression and brevity old-fashioned, increased expense, and often swamped bench and bar alike by the quantity rather than the quality of material offered for consideration.

"Motions to expunge and limit cross-examination should have been made in these cases, though they are feeble remedies exposing counsel to personal reproach, and rendering judges afraid of keeping out of evidence what they cannot (on motion at all events) understand. *But the radical difficulty of which this case is a striking (though not singular) example will remain as long as testimony is taken without any authoritative judicial officer present and responsible for the maintenance of discipline and the reception or exclusion of testimony.*"

wealthy antagonists. Indeed, I know of an interference case which has been going on for the last six or seven years, and which has already cost one of the contestants over $60,000. Even after the interference case is decided in one's favor, one has to take all the ordinary chances of further expensive infringement suits. Is this to the benefit of the public, for whom primarily, our laws are created? Let us see: The public wants as early as possible a disclosure of any invention, and with that end in view, the patent law stimulates such disclosures by offering, as reward, 17 years of patent monopoly. Yet everybody knows that our interference system hopelessly delays the publication of an invention. Furthermore, our interference rules are in many ways a terrifying menace to the industries of the country.

For instance, a man applies for a patent. The patent is allowed and published. On the strength of this patent, a company is formed, which goes ahead, builds an expensive factory, and starts operations. Then, it has frequently happened that an interfering patent application, which was not known to exist at the time the company was organized, embodies identical claims, and is put forward in objection to the published patent. This may invalidate the patent on which the company was formed, and thus stop and annihilate an enterprise which was begun entirely in good faith, and on a sound basis. Such a thing is impossible with the German system, where the first applicant, unless his application is based on fraud or theft, gets the patent, as long as no one else can prove prior use or prior public disclosure. Rigid examination, followed, after allowance, by a short period for public objection, make the German proceedings relatively inexpensive, and give added value and prestige to patents issued under this system.

It may be objected to this system that it induces filing an application before the invention is sufficiently ripe, but even with our system, the same objection holds good. Furthermore, with our current methods, it is possible to file patents and let them pend for many, many years, and use these pending applications as a drag-net in which to catch any other patents which may be applied for by others, and by which to get the benefit of any practical developments or improvements which go on in the meantime; this was clearly demonstrated in the famous Seldon case.

For deciding priority in purely scientific publications, it has been accepted, since the time of Humphrey Davy, that "priority of publication, unless in case of fraud, means priority of conception." This simple rule, if applied to the Patent Office system, would sweep away the most complicated and most expensive part of our Patent Office methods. At the same time, it would stop an interpretation of our patent law, which is decidedly dangerous and unfair to the unsuspecting public, and has no advantage to the inventor, unless he be rich, or unless he be propped by wealthy backers.

All these reforms, or improvements, whatever you want to call them, are relatively simple and might have been obtained long ago, if the real interested parties, the public and the inventors, had demanded them. If we unite in our demands we can surely obtain them.

To the honor of the better class of lawyers, let me mention that the Patent Law Association of Washington is doing good work to accomplish some much needed reforms. Lately, in conjunction with the American Institute of Chemical Engineers, and the Inventors' Guild, a start has been made towards awakening the interest of our national engineering societies. Let us all join in this movement. Let us not overlook the fact that out legislators need as much education on this subject as the public-at-large. But if we try to suggest reforms, let us be practical and first concentrate our efforts on those reforms upon which we can all agree. Let us avoid theorizing or dreaming. A perfect patent law will never exist, except perhaps in heaven, where all men are angels. Then patent laws, as well as other laws, can be dispensed with—but we are still on the earth and for a long time.

Remember that if there is much to criticize in our patent system, there exists the same chaos in our civil and criminal laws, which badly need a general overhauling.

We chemists or engineers are apt to forget that if Science, Engineering, and all achievements based on exact knowledge and sound reason, have made immense progress in late years, our laws and the administration thereof, have advanced little beyond what they were two or three thousand years ago, so that they are now an anachronism ill adapted to our modern conditions of life. But most judges and lawyers, when they talk about dispensing justice, have acquired, like the Chinese Empire, the habit of looking backwards for "precedents," which for them still remain the most respectable and the most imposing arguments.

At this time, the immediate danger for our patent system is that some congressmen or senators, ignorant of the real situation but anxious to advertise that they want "to fight the trusts," will rush through bills which will work untold harm to our patent system and to the industrial progress of our country. Some of the many patent bills now before Congress sadly illustrate the unpreparedness of their happy-go-lucky originators. Our congressmen and senators should know that the best anti-trust remedies are those which stimulate individualism and private enterprise and nothing works so strongly to that effect as liberal patent laws, provided such laws can be enforced by the patentee of moderate means instead of securing only the interests of wealthy corporations.

Why could this intricate subject of patent reform not be submitted to a competent commission created by the president? This commission, before suggesting or endorsing reforms, should consult with representatives of our national technical and engineering societies, as well as with manufacturers, business men, representatives of the Patent Office and lawyers. A resolution to that effect has recently been addressed to the President of the United States by the Inventors' Guild.

ORIGINAL PAPERS

SOME RECENT DEVELOPMENTS IN WOOD DISTILLATION.[1]

By Thos. W. Pritchard.

In taking up the subject of wood distillation, I wish to say in the beginning that, like every one else, I am subject to correction and am anxious to profit by the experience of others. It is only by so doing that we accomplish anything. There have been many improvements in the art of wood distillation since I first began the work, and I know of no industry which, in so short a time, has made such marked strides and which merits so much investigation and criticism.

In 1904 I prepared a paper for the *Scientific American Supplement*, in which I gave credit for the first commercial work in the distillation of Pine Wood to James Stanley, who built a small commercial plant in Wilmington, N. C., in 1872. This plant was not a success in the hands of Stanley, and was shortly after taken over by two gentlemen of Danish birth, who were somewhat familiar with similar work which was being carried on in their Motherland. One of these men is still living and is actively engaged in the work to-day. I speak of Mr. L. Hanson, who is President of the Spirittine Chemical Company, of Wilmington, N. C.

It is rather a striking coincidence that the first, and I may say the last plant, has been built in Wilmington, and the last one within a few feet of the former location of James Stanley's plant. This last plant, which is by my process, I shall describe later.

The process, as started by Stanley and carried out by Mr. Hanson, was the old crude method of Destructive Distillation, which consisted of a series of retorts with condensers attached, set up in brick work with furnaces beneath. The wood was placed in the retorts and the doors closed, fires were started in the furnaces and kept up until distillation ceased; the retorts were then allowed to cool and the charge was withdrawn. No attempt was made to control the temperature during distillation and it was not until years later that the possibilities of varying products, depending on the temperatures, were thought of. By this old method, many different degrees of heat existed in the retort at the same time, and it was a noticeable fact that the top of the retort was many degrees hotter than the bottom or sides; the loss of heat was very great as it was necessary to heat up the brick-work before distillation started. There was no attempt at first to refine or separate these products; they were pumped into storage tanks and used for the preservation of timber, a creosoting plant having been built nearby, and the creosoting of timber was a part of the Company's business.

I do not believe that any one, at this time, even thought of the possibilities of there being turpentine in the products of distillation. I can well recall the time when such a theory would have been hooted at. I believe that we can safely give credit to the steam process people for the possibilities of the turpentine extraction from fat pine wood. I do not remember its production prior to their activities, and certainly not of good quality and in commercial quantities. This steam process with its variation held out many possibilities to us all at first, but I regret to say that, from my own observation, it has not proved commercially successful, save in a few cases.

Within the last few years still another process has been evolved, which, while not new, still, as applied to the extraction of the products from pine wood, was novel. I refer to the solvent process, for which great things are claimed.

By this process the wood to be treated is first shredded, or hogged, as it is called, and then subjected to the solvent action of naphtha or some other volatile solvent. The solvent combines with the resinous extracts and the resultant liquid is then drawn off and subjected to a fractional distillation. The solvent is recovered and the products are then refined. The solvent process is claimed by many to be the most profitable, and I know that large sums are being spent for the erection of plants using this process. I have always held, however, that there is but one method for the utilization of wood waste in the form of fat light wood; and that is to completely utilize the raw material. In no other industry would we find such a condition as exists where the steam process and the solvent process are in operation.

The taking of a raw material and the extraction of but a proportionately small part of its valuable contents and then throwing the remainder away, is a poor proposition, no matter how you look at it. I believe that every man who has ever turned his attention to this art, has realized from the beginning that the one great essential to be sought was temperature control during all times of the distillation. Many methods have been tried to solve this question and I feel reasonably sure that it has at last been successfully worked out.

I refer now to the plant I have just completed for the National Wood Distilling Company, of which I am an officer. In describing this plant and the methods used, I ask that I be allowed to indicate the weak points in the other processes, as each of these was of assistance to me in developing the new and successful process we have.

Let us take up the old destructive process and see how it bears a rigid analysis: First, for its good points (and I wish to say here that nearly every plant that has been a financial success has been of this type) the destructive process does utilize the raw material and it does produce far greater yields than any other process, the average production from a cord of good wood by the old destructive process being approximately twenty gallons of turpentine, ten gallons of light oil and seventy gallons of heavy oil, with a residu

[1] Read before the New York Section of the Society of Chemical Industry, March 22, 1912.

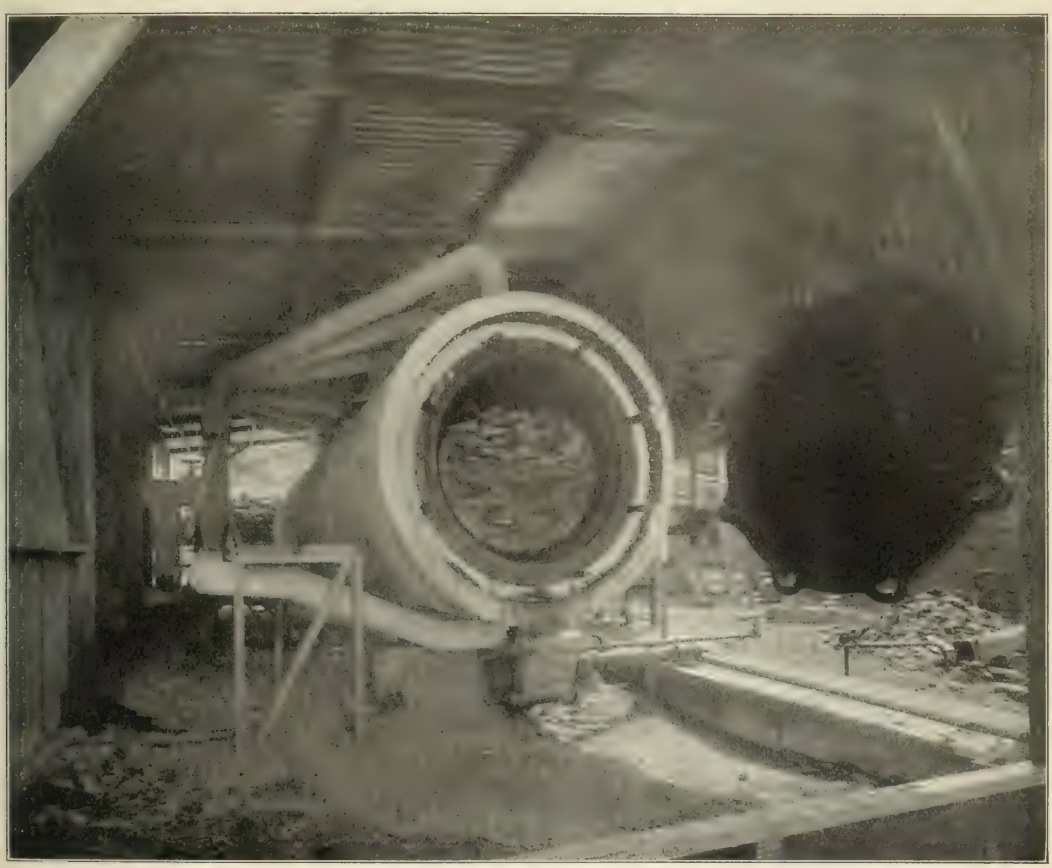
of twenty-five bushels of charcoal to the cord. I do not include either alcohol or acetic acid, as their value is slight and varied, and I may say that very few plants distilling resinous woods have found it of advantage to utilize these products.

The first cost of this style of plant is not great in comparison with others, and the expense and difficulty of hogging wood is not a factor.

The weak points in this process are, however, serious defects: First, the lack of temperature control in the retort results in the formation of all sorts of compounds which distil with the turpentine and contaminate it; and this same lack of heat control results in a large percentage of the heavy products being burned in the retort. Any one who has ever operated a plant of this type will readily recall the deposit of carbonized matter which has to be cut out of the retort after a short usage. Secondly, the very high temperatures to which the average destructive plant is subject means a comparatively quick wear-out and very heavy up-keep, as well as an enormous waste of fuel. Third, the fire risk in this style of plant is very great, so high in fact, that no insurance company will accept a plant of this type as a risk.

In summing up the good and bad points we may say that the old style destructive process gives us good yields at comparatively low cost, but the products are of inferior quality, the cost of maintenance high and the fire risk great. In addition to this is the factor of time, as it takes very much longer to handle a quantity of wood by this process than by others.

In considering the steam process, we must give it credit for the quality of turpentine produced, and for the essential idea in wood distillation, the temperature control. We must, however, admit that a weak point in this process is the very small proportionate yield of products; secondly, that it does not utilize the raw material to the fullest extent, as a major part of the products of the wood are not extracted, thus necessitating the use of an enormous quantity of raw material to accomplish any great results.



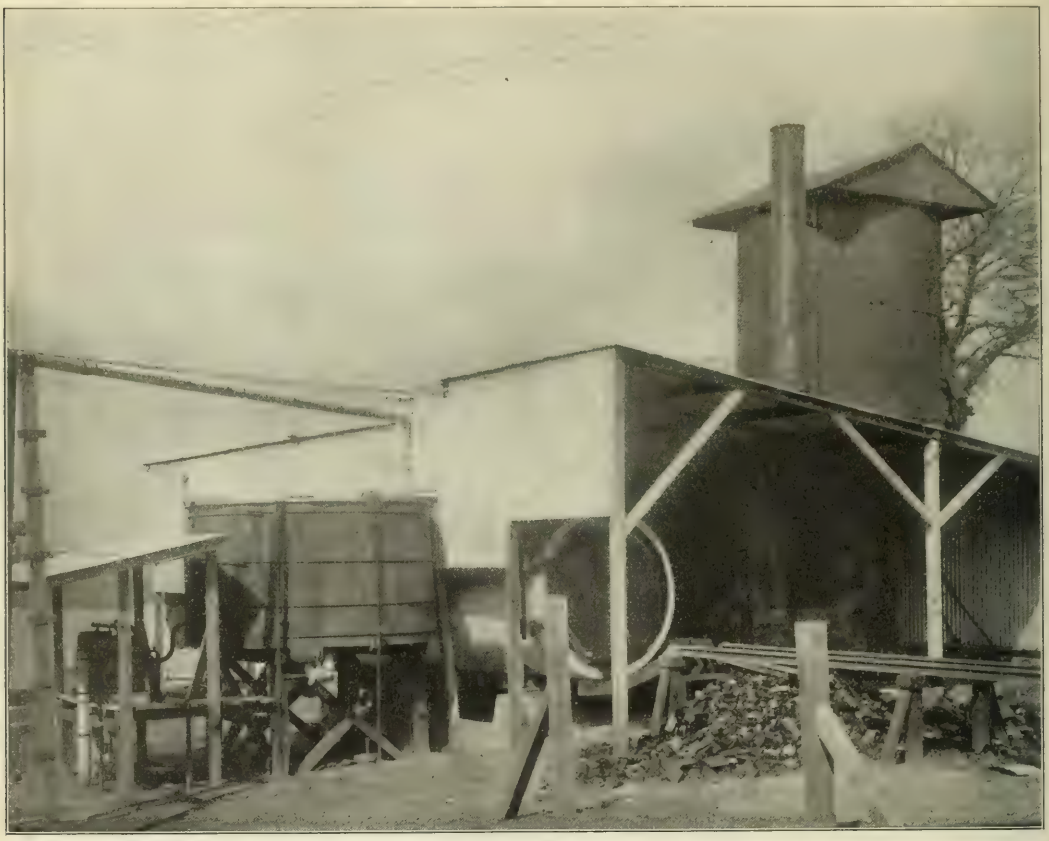
Commercial Plant Retort

There have been all sorts of claims as to the quantities produced by this process, but after very careful investigation, based on the report of men who are engaged in this line of work, I am forced to the conclusion that from six to fifteen gallons of turpentine, and from two to four gallons of pine oil is the minimum

and maximum yield for a cord of fat wood, the variations in quantity being due to the difference in quality and treatment.

The expense of production by the steam process is high; the waste of raw material is enormous and without reason. We may, therefore, grant to the steam process an excellent quality of products, with safety of operation so far as fire is concerned, and at the same time we must condemn it for the poor yields, cost of operation and waste of raw material.

Within the last few years still another process has been evolved. I refer to the Solvent Process, for



Commercial Plant—Showing Storage Tank Condensers, Etc.

which great things are claimed. I am inclined to think from what I can learn that the solvent process possesses considerable advantages over the steam process in quantity of production. I also believe that the quality of the turpentine is equally as good, and this process also produces a good yield of rosin. There is still, however, the objectionable feature of a very high fire risk, comparatively high cost of operation and failure to completely utilize the raw material.

The ideal process for the distillation of wood, we may then admit, must possess the following essential features: First, definite control of the temperature during the entire process of distillation; Second, a maximum yield of products; Third, products must be of good quality; Fourth, cost of operation must be comparatively low; and Fifth, the fire risk must be minimized as far as is possible.

I am going to try to describe a plant which we have recently built in Wilmington, N. C., within a few feet of the original plant of James Stanley.

When I first began work on wood distillation, I realized that temperature control was the one great issue. I tried experiment after experiment to achieve this, and at last discovered that by utilizing the old chemical process of the oil bath, I could get very definite temperature control at comparatively high temperatures. I had great difficulty for a long time in getting an oil which would stand repeated heating without cracking. I finally found, however, a very high fire-test petroleum cylinder stock, which could by heated to six or seven hundred degrees F., without trouble, provided air was excluded. With this fact as a starter I developed our present process, which I will now try to describe.

I can best do this perhaps, by first describing a miniature plant complete, which I had built last year, and in which I ran continuously ninety-six charges. In the construction of this small plant, I

used two pieces of pipe: the inner shell was eight inches in diameter by twenty-four inches in length; the outer shell enclosed this, leaving an intermediary space of one-half inch. The ends of this space, of course, were tightly closed. From the inner shell an outlet pipe passed through the space and through the outer shell and connected with an ordinary worm, the condenser. Into the bottom of the outer shell at one end entered a half-inch pipe, with the take-off at the bottom at the other end. Connected with this entrance pipe was a small gas hot-water heater, and from the bottom of this hot-water heater, a pipe led to a small rotary pump, and from the pump to a small steel storage tank. The outlet pipe from the bottom of the outer shell opposite end of the inlet pipe led directly to the top of this storage tank, which was enclosed. By means of the small rotary pump, the bath oil contained in the storage tank was forced through the gas hot-water heater, taking the place that would originally be occupied by the water in the same, and from there went into the intermediary space entering at the bottom, and was circulated around the inner retort, finding its outlet at the bottom of the outer shell farthest away from the inlet, from there passing back to the storage tank through the pump around the retort and so on, thus keeping a continual circulation. Between the inlet pipe and outlet pipe I had a pipe of similar size connected with suitable valves, so that the oil could be by-passed and the retort circulation completely cut off. I also had a reserve tank filled with cold oil, which allowed me to introduce cool oil into the circulation at any time. By means of increasing or decreasing the speed of the pump, opening or closing the valves used by passing or introducing cold oil into the circulation, I found it entirely practicable to control the temperature absolutely.

We used in this small retort twenty pounds of wood at a charge, and estimating the weight of a cord of good rich wood at four thousand pounds, we had no trouble in getting a pretty accurate approximate average of the production by this process. I must confess that the results of this experimental plant were far beyond our most sanguine expectations. We kept a record of every charge and our average for fifty charges was thirty-six and a fraction gallons of water white turpentine, ten gallons of light oil, and one hundred and twenty-five gallons of heavy oil.

I have with me one or two of these record sheets which I shall be glad to show. We found that we had no trouble whatsoever in getting complete and uniform carbonization, so complete, in fact, was the heat distribution by this method that a solid stick of timber eight inches in diameter and of the length of the inner shell was charred through and through.

In operating this model we discovered that by varying the temperatures, we could produce varying products. We also discovered that by drawing off the liquid contents of the retort after the turpentine had been distilled we could produce large quantities of an excellent grade of rosin. In fact, one of the main features of this process is its extreme flexibility.

Our commercial plant, which we have just completed and which is now in daily operation, is an exact duplicate of the model, except for the fact that the space for the bath oil is proportionately about three times as great. The large retort has an outside diameter of five feet, with an inner shell of three and a half feet, and a length of twenty-eight feet. This gives us nine inches of oil space between the inner and outer shells.

For heating the oil bath we use a continuous coil of electrically welded pipe, containing 350 lineal feet. This pipe is set in a specially constructed furnace so that while not in direct contact with the fire, it yet gets a maximum amount of the heat. The results of this large retort have checked absolutely with the model, and we see no reason why it should not continue to do so indefinitely. I used the same oil bath in the model for ninety-six continuous charges, and, so far as we are able to tell, the bath oil is in exactly the condition to-day as when first put into service. The low cost of this oil and its long service make it an ideal menstruum for conveying the heat.

In operating this plant, we run the wood into the inner shell of the retort on cars, the doors are closed, and a steam jet is opened with leads into the inner shell. This is done to force out the cold air and so hasten the heating. The oil bath is then circulated from the storage tank by means of a low pressure pump through the heating coil, and so to the retort where it fills completely the space between the inner and outer shells forming a blanket of hot oil with a uniform temperature, passing out at the bottom of the retort and back to the storage tank. We control the temperature so that the inside heat shall not exceed 450 degrees F., until we have distilled off all the turpentine and pine oil; we then allow the temperature to slowly rise until we have fractionated the light oil, and it is just at this point that destructive distillation begins and fractional distillation ceases. We find that at approximately 480 degrees F. we begin to get the distillates with the distinctive empyreumatic odors. The temperature is held below 525 degrees F. until all the light oil is over and then allowed to increase as fast as possible. We find that at a maximum temperature of 610 degrees F. in the inner shell, we can get complete distillation of all the products, leaving us dry charcoal of excellent quality. At this temperature we find that our bath oil is at a temperature of 650 degrees F., which is as high as we generally carry it, though we have gone as high as 750 degrees F., without trouble. I do not hesitate to say that this process is the most accurate, and the apparatus the most scientific ever evolved for this work, and the results prove it.

At no stage of the process is it not under perfect control and the temperature can be raised or lowered at will. We have found by actual tests that we can hold the temperature of the oil bath at any given degree as long as may be desired. The time consumed in running a charge by this process is comparatively shorter than by any other; it takes longer than a steam process plant, but when the difference in the

production is taken into account, this comparison is in our favor. We actually begin distillation as soon as the wood goes into the retort, as the oil bath is carried to about three hundred and fifty before the cars of wood are run in. After the charge is over, instead of having to wait many hours for the retort to cool, we mechanically assist the cooling by pumping cold oil through the heating chamber.

The fire risk is also a slight danger by this process, and I may say right here that an examiner for one of the leading companies in America has classed our plant as a comparatively safe risk, and is willing to write us at a very fair rate of insurance. In regard to the quantity and quality of the products produced by this method, let me say that both the turpentine and oils are of a very high grade as the samples I have with me show. The analysis of the turpentine shows it to be of remarkable quality. The production is far greater than by any other process with which I am familiar. This is best shown by the records of charges which show not only the yield but the temperature at which each product was distilled.

This daily record gives an absolutely accurate record of the varying temperatures, both of the oil bath and the inner shell or distilling space. We also get the exact periods and temperatures at which the distillates change in nature. We may, therefore, grant that we have accomplished: first, temperature control; second, the complete utilization of the wood; third, a maximum amount of products.

This being granted, let us see what the quality is, and also consider the cost of production. In taking up the question of quality, I wish to say that it is hardly a fair comparison to consider the products made by this process against the old destructive ones, as they seem distinctly different. The turpentine as the following analysis shows is very close to the very best gum turpentine, so close, in fact, that but for one feature it would be indistinguishable; I refer now to the pine oil contents which I may say is the one means of classifying wood turpentine as against gum turpentine. The presence of this product, even in very small quantities, raises the average of the boiling points in fractionation. I believe I am correct when I say that this is the one distinction in even the very best wood turpentine. I am glad to say that I am now working on a method of refining which seems to promise an easy and economical method of extracting even the slightest quantity of pine oil from refined turpentine. If this can be accomplished, I do not believe it will be possible to distinguish good wood turpentine from that distilled from the crude gum turpentines.

The following analysis of our unrefined product was made by J. E. Teeple, of New York City:

Color—slightly yellow.
Leaves no stain on paper.
Specific gravity at 16° C.—0.865.
Distillation 50 per cent. at 160° C.
Distillation 80 per cent. at 163° C.
Distillation 85 per cent. at 164° C.
Distillation 90 per cent. at 165.5° C.
Distillation 95 per cent. at 172° C.
Non-volatile matter at 100° C.—0.03 per cent.
Flash-point—168.5° F.
Insoluble in sulphuric acid 2.5 per cent.

Odor—Contains a noticeable odor foreign to turpentine and very similar to creosote. This odor is usually removed by shaking with dilute alkali.

The turpentine is slightly acid but this acidity is easily removed by shaking with dilute alkali.

Iodine absorption No. 375.

In comparing the oils produced by this process, I cannot do better than to show samples of each of the distillates, both in crude form and as we refine them. It will be noticed that the heavy and light oils are very much brighter in color, and have a much milder odor than the ordinary destructive distillates. This is due in part to the fact that they are not burned, and are taken from the retort at their normal distilling temperatures. I have many times seen oils made by the old destructive process so black in color and so high in odor that they were hardly worth marketing, and this was unquestionably caused by exposure to excessive temperatures. I want especially to call your attention to the samples marked "X", "XX," and "XXX" oils, also the one marked "XL." These oils are the products of special processes of refining which we have worked out, and they seem to compare very favorably with the better grades of rosin oil. They do not, however, analyze as such. We have had these oils tested out for the commercial purposes that rosin oils are used for, and they seem to serve admirably. They can be produced at much less cost.

The oil marked "XL" is worthy of notice because of the fact that it is practically odorless. In addition to this, it seems to have rather remarkable drying properties, and made into paint shows excellent wear. We have had paint samples in service for seven months or more, and the results as compared with pure linseed are very favorable indeed. Only the darker shades could be produced, however, as the oil darkens any light pigments. There is no question but that this oil will be of great value in making up a cheaper grade of paints for such purposes as freight cars and rough work generally.

In speaking of the refining of the oils produced from the distillation of pine woods, I would like to say that hardly anything has been done. I have perhaps gone as far along this line as any one, and have made, perhaps, as many as seventy-five distillates. I believe that this work alone offers a wonderful field for the research chemist, and it has always been a matter of wonder to me that some of our men who have the time and means to take this up, have not done so. I feel sure that no field before us to-day offers greater opportunities for discovery. The subject is so vast in scope that it is with great difficulty that I have been able to limit my paper to a reasonable time.

I feel that I cannot close without saying just a few words relative to the possibilities of the distillation of pine wood. There are to-day millions of cords of wood lying on the ground rotting, and there is a money

value of approximately twenty-five dollars in each and every cord of this wood. There are every day thousands of cords of rich pine wood burned at sawmills that have an equal money value.

The distillation of pine wood is not an industry which requires large capital. Plants may be built for comparatively small amounts that will pay good dividends. There is an unlimited demand for all the products and at prices which will pay handsomely. Many plants have failed, it is true, but every failure can be safely attributed to lack of knowledge of the industry, lack of capital or a poor process. Many men have gone into the business thinking that they could get fancy prices for the products and have been disappointed. A steady sale at a reasonable profit is all that can be expected. There is, however, a steady demand for all of the distillates now, and this demand is growing daily. The question of timber preservation has become a vital one, and when the fact that the heavy wood oil is even more valuable than dead oil of coal tar for this purpose becomes generally known, there will be an unlimited demand for this product.

I have had offers from users of timber preservatives for very large quantities of the heavy wood oil, provided it could be furnished in sufficient quantity and at a low price. So far this has been out of the question, as one large R. R. System could take all the oil made in this country. There is one feature of the industry which has done more to militate against it than anything else. I refer now to the lack of coöperation among the men engaged in the work. Every one thinks that he has a little bit more knowledge than any one else, and is jealous of it.

An association which would allow of an exchange of ideas and promote a spirit of helpfulness would do more for the art than any other one thing. Trade secrets need not be divulged, but matters of moment for the good of all could be promoted by such an organization, and only by such.

Typical Experimental Tests.

Charge No. 19—April 25, 1911.
20 lbs. wood (good).

		Inside.	Outside.	
7.30 A.M.	Fire started			
8.30 "	Turps. started	380°	510°	
9.00 "		395	477	32 ozs. turps.
10.00 "		413	480	
11.00 "		451	556	
12.00 M.		484	567	
1.00 P.M.	Turps. stopped			
	Light oil started	494	578	9 3/4 ozs. light oil
2.00 "		508	590	
3.00 "	Light oil stopped			
	Heavy oil started	572	675	
4.15 "		581	666	50 oz. heavy oil
5.00 "		597	690	
6.00 "		595	675	

Calculated to Cord Basis.

Charcoal	30 bushels
Residue	20 gals.
Crude turps	50.0 gals.
" light oil	15.23 "
" heavy oil	78.12 "
	143.35 "

Charge No. 26—May 3rd, 1911.
20 lbs. wood.

		Inside.	Outside.	
7.40 A.M.	Fire started			
8.40 "	Turps. started	380°	510°	
9.00 "		387	507	
10.00 "		420	510	25 ozs. turps.
11.00 "		428	522	
12.00 M.		467	565	
1.00 P.M.	Turps. stopped			
	Light oil started	490	578	6 1/4 ozs. light oil
2.00 "	Light oil stopped			
	Heavy oil started	536	641	
3.00 "		570	678	
4.00 "		596	678	68 ozs. heavy oil
5.00 "		594	674	
5.30 "		592	680	

Calculated to Cord Basis.

Charcoal	25 bushels
Residue	30 gals.
Crude turps	38.06 gals.
" light oil	10.15 "
" heavy oil	106.25 "
	154.46 "

Charge No. 11—April 15, 1911.
20 lbs. wood (good).

		Inside.	Outside.	
9.30 A.M.	Fire started			
10.00 "		270°	430°	
10.30 "	Spirits started	345	525	
11.00 "		374	489	
12.00 M.		378	436	
1.00 P.M.		384	435	24 ozs. spirits
2.00 "		385	430	
3.00 "		392	432	
3.25 "	Rosin started	387	416	(Rosin 2 1/4 lbs.)
3.55 "	Rosin stopped	395	455	
4.00 "		408	508	
5.00 "		520	615	
5.10 "	Stop fire	528	628	

Calculated to Cord Basis.

7 oz. light oil on cooling down:

Wood left	12.0 lbs.
Residue	4.0 ozs.
Crude turps	37.44 gals.
" light oil	...
Rosin	500.0 lbs.

Charge No. 15—April 20, 1911.
20 lbs. wood (good).

		Inside.	Outside.	
8.10 A.M.	Fire started			
9.00 "	Spirits started	372°	500°	
10.00 "		408	484	
11.30 "		435	535	24 1/4 ozs. spirits
12.00 M.		452	550	
1.00 P.M.		500	600	
1.15 "	Spirits stopped			
	Light oil started	508	623	7 1/2 ozs. light oil
2.00 "		540	650	
2.20 "	Light oil stopped			
	Heavy oil started	550	662	
3.00 "		574	677	
4.00 "		595	680	60 ozs. heavy oil
5.00 "		607	692	
5.25 "		605	690	

Calculated to Cord Basis.

Charcoal	28 bushels
Residue	20 gals
Crude turps	38.2 gals.
" light oil	11.7 "
" heavy oil	93.6 "

Charge No. 39—May 13, 1911.

20 lbs. wood

		Inside.	Outside.	
[illegible]	[illegible]	[illegible]	[illegible]	
8.15	Turps. started	344°	489	
9.00		363	473	19½ ozs.
10.00		405	490	turps.
11.00		415	483	
12.00 M.		465	560	
12.15 P.M.		502	598	6 ozs.
1.00 "		508	602	light oil
2.00 "		535	620	
3.00 "		575	661	67 ozs.
4.00 "		610	670	heavy oil
8.00 "		608	660	
8.30 "		600	650	

Calculated to Cord Basis.

Charcoal	28 bushels
Residue	20 gals.
Crude turps	30.46 gals.
" light oil	9.37 "
" heavy oil	104.68 "

Charge No. 40—May 19, 1911.

20 lbs. wood.

		Inside.	Outside.	
7.15 A.M.	Fire started			
8.30 "	Turps. started	376°	485°	
9.30 "		430	520	
10.30 "		465	526	20½ ozs.
11.30 "		476	544	turps.
12.30 P.M.		485	541	
1.30 "		512	583	
2.30 "		550	640	10 ozs.
3.00 "		580	672	light oil
4.00 "		596	675	67 ozs.
5.00 "		612	674	heavy oil
5.30 "		610	670	

Calculated to Cord Basis.

Charcoal	28 bushels
Residue	15 gals.
Crude light oil	15.62 gals.
Crude turps	32.03 "
Crude heavy oil	104.68 "

Charge No. 47—May 27, 1911.

20 lbs. wood.

		Inside.	Outside.	
7.00 A.M.	Fire started			
8.15 "	Turps. started	400°	480°	
9.00 "		429	508	
10.00 "		460	525	27½ ozs.
11.00 "		492	565	turps.
12.00 M.		502	596	
1.00 P.M.		545	622	5½ ozs.
2.00 "		562	642	light oil
3.00 "		573	637	
4.00 "		605	685	62½ ozs.
5.00 "		600	676	heavy oil

Calculated to Cord Basis.

Charcoal	28 bushels
Residue drawn off	40 gals
Crude turps	42.96 gals.
Crude light oil	8.59 "
Crude heavy oil	97.65 "

Charge No. 50—May 31, 1911.

20 lbs. wood.

		Inside.	Outside.	
7.00 A.M.	Fire started			
8.05 "	Turps. started	388°	508°	
9.00 "		425	520	
10.00 "		455	540	32 ozs.
11.00 "		481	571	turps.
12.00 M.		501	583	
12.20 P.M.		515	600	7 ozs.
1.00 "		532	611	light oil
1.30 "		543	643	
2.00 "		572	655	65 ozs.
3.00 "		610	684	heavy oil
3.30 "		614	675	

Calculated to Cord Basis.

Charcoal	30 bushels
Residue drawn off	20 gals
Crude turps	80.60 gals.
" light oil	10.93 "
" heavy oil	101.86 "

Charge No. 58—June 9, 1911.

20 lbs. wood.

		Inside.	Outside.	
8.10 A.M.	Fire started			
9.20 "	Turps. started	374°	500°	
10.00 "		436	543	
11.00 "		476	566	23½ ozs.
12.00 M.		517	607	turps.
12.30 P.M.		526	617	
1.00 "		540	632	7 ozs.
1.30 "		552	641	light oil
2.00 "		563	648	
3.00 "		600	677	66 ozs.
4.00 "		608	680	heavy oil
4.30 "		600	670	

Calculated to Cord Basis.

Charcoal	28 bushels
Residue drawn off	20 gals.
Crude turps	36.71 gals.
" light oil	10.93 "
" heavy oil	103.12 "

Charge No. 79—July 5, 1911.

20 lbs. wood.

		Inside.	Outside.	
7.30 A.M.	Fire started			
8.36 "	Turps started	385°	508°	
9.00 "		411	522	
10.00 "		449	536	28½ ozs.
11.00 "		474	556	turps.
11.55 "		497	591	
12.57 P.M.		546	636	6¾ ozs.
2.00 "		590	677	light oil
3.00 "		598	681	72 ozs.
3.35 "		600	682	heavy oil

Calculated to Cord Basis.

Charcoal	4¼ lbs.
Residue	2½ "
Crude turps	44.53 gals.
" light oil	11.54 "
" heavy oil	112.50 "

Charge No. 82—July 10, 1911.

20 lbs. wood.

		Inside.	Outside.	
7.10 A.M.	Fire started			
8.20 "	Turps. started	384°	495°	
9.00 "		409	512	33 ozs. turps.
10.00 "		448	551	29 ozs. water
11.00 "		477	560	
11.40 "		498	593	9 ozs. light oil
1.00 P.M.		542	630	10½ ozs. water
1.10 "		546	631	
2.00 "		575	667	50 ozs. heavy oil
3.00 "		584	661	26 ozs. water
4.00 "		579	644	

Calculated to Cord Basis.

Charcoal	30 bushels
Residue	35 gals.
Crude turps	51.56 gals.
" light oil	14.06 "
" heavy oil	78.12 "

Charge No. 90—Aug. 12, 1911.

20 lbs. Western wood.

		Inside.	Outside.	
8.25 A.M.	Fire started			
10.08 "	Turps. started	397°	473°	Fuse burnt out
11.00 "		414	477	38¼ ozs. turps.
12.00 M.		439	495	
1.00 P.M.		459	511	27 ozs. water
2.00 "		486	562	10 ozs. light oil
3.00 "		551	622	5½ ozs. water
4.00 "		606	702	
5.00 "		637	682	90 ozs. heavy oil
5.30 "		631	686	32 ozs. acid

Refined Products.	Gals.
W. W. turpentine	40 0
Second turpentine	1 5
Light oil	10 5
Light product, No. 1	3 1
Light product, No. 2	2 7
Heavy oil	87 5
Refined to extra heavy oil	40 6
	185 9

Calculated to Cord Basis.

Charcoal	950 lbs.	44 lbs.
Residue	138 "	11 ozs.
		Gals.
Crude turps		80 39
" light oil		15 62
" heavy oil		110.62

Tests on Commercial Plant

Charge No. 1—March 19, 1912.

4653 lbs. wood.

Time.	Changes.	Temperature. Retort.	Oil.	Output.
5.15 A.M.	Pumps started			
6.30 "	Steam turned in retort			
6.43 "		226°		
8.00 "	Oil turned in retort below	260		
8.00 "		217		
8.17 "	Steam cut off	217		
9.15 "		218		
10.07 "		225	272°	33 gals. turps.
10.15 "	Cut out tank			
11.05 "		255	315	
12.00 M.		276	345	
1.00 P.M.		309	393	
2.00 "		332	440	
3.00 "		366	477	
4.00 "		380	520	
5.00 "		425	549	
5.20 "		445	559	
6.12 "		480	587	20 gals. light oil
6.30 "		486	596	
8.34 "		502	605	
9.35 "		550	631	
10.33 "		563	646	
11.34 "		575	649	
12.33 A.M.		562	646	86 gals. heavy oil
1.35 "		558	643	
2.22 "		559	643	
3.30 "		555	645	
3.55 "		557	645	

Charge No. 2—March 21, 1912.

1-cord slabs—5076 lbs.

Time.	Changes.	Temperature. Retort.	Oil.	Output.
6.50 A.M.	oil and steam on			
7.10 "	Steam cut off	210°		
8.00 "		181	259°	
9.00 "		191	272	
10.00 "		226	326	
11.00 "		262	356	
11.43 "	Dist. started	286	377	
12.00 M.		283	384	
1.17 P.M.		290	415	
2.00 "		300	423	
3.00 "		285	430	
4.05 "		296	442	
5.05 "		300	455	33 gals. crude turps.
6.00 "		325	467	
7.00 "		377	478	
8.00 "		389	488	
9.00 "		402	495	
10.00 "		405	500	
11.00 "		411	500	
12.03 A.M.		415	507	
1.00 "		422	511	
2.00 "		431	516	
3.00 "		437	527	
4.00 "		448	535	
4.35 "	Dist. changed	457	541	
5.00 "		465	542	
6.00 "		480	555	10 gals. light oil
7.00 "	Dist. changed	498	563	
8.00 "		502	568	

Charge No. 2—*Continued.*

Time.	Changes.	Temperature. Retort.	Oil.	Output.
9.00 A.M.		504	576	
10.00 "		504	587	79.29 gals heavy oil
11.00 "		512	599	
12.00 M.		504	604	
12.45 P.M.	Charge stopped, leaky pipe			

47.21 gals. pitch

Charge No. 3—March 25, 1912.

1 cord slabs—4508 lbs.

Time.	Changes.	Temperature. Retort.	Oil.	Output.
6.30 A.M.	Steam on for 3 min.			
6.33 "	Oil started in retort	218°	300°	
7.00 "		175	295	
8.00 "		218	318	
9.00 "		240	347	
10.00 "		268	368	
10.30 "	Dist. started	294	377	
11.00 "		306	382	26 gals. crude turps.
12.00 M.		321	400	
1.00 P.M.		335	427	
2.00 "		348	455	
3.00 "		394	477	
4.00 "		409	492	
5.00 "		428	513	
6.00 "		451	532	
7.00 "		469	543	
8.00 "		483	561	71½ gals. crude light oil
9.00 "	Dist. changed	500	570	
10.05 "		525	589	
10.30 "	Dist. changed	533	595	
11.00 "		540	606	
12.00 M.		549	616	44 gals. heavy oil
1.00 P.M.		556	627	
2.30 "		559	648	

42.38 gals. pitch

National Wood Distilling Co.,
Wilmington, N. C.

SOME PROBLEMS IN CHEMICAL ENGINEERING PRACTICE.[1]

THE MANUFACTURE OF CHLOROFORM FROM BLEACHING POWDER AND ETHYL ALCOHOL.

By F. W. Frerichs.

Received January 5, 1912.

As an example of improving an established process of manufacture, I have selected some work which I did about thirty years ago in connection with the manufacture of chloroform. At that time chloroform was made from tax-paid alcohol and bleaching powder. The acetone process was then little known but was developed about five years later superseding the alcohol process on account of its greater cheapness. But since we now have tax-free alcohol for manufacturing purposes, the old process has gained interest again, and this is one of the reasons why I have looked up old records in order to show what can be done with the alcohol process.

In the year 1883 I was in charge of a chloroform plant, comprising six cylindrical stills standing on end, each still being 6 feet in diameter and 8 feet high. Each still was connected with a condenser consisting of a lead coil and a receiver to catch the resulting chloroform. A flat iron box, to mix the bleaching powder with water, was over each pair of chloroform stills. The general arrangement of the apparatus was as given in Fig. 1.

[1] Address read at the Annual Meeting of the American Institute of Chemical Engineers, in Washington, D. C., December, 1911.

The apparatus was operated in the following manner:

1000 lbs. of bleach having 35 per cent available chlorine, or its equivalent, were dissolved in the square box A (Fig. 1) in sufficient water to make about 25 cu. ft., and the solution was

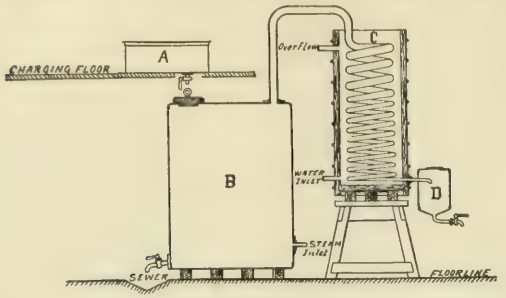


FIG. 1.

run off into still B, a small quantity of water being used to wash the box. Eight gallons of 94 per cent. alcohol by volume were added, whereupon the still was closed and left to stand over night.

LIST OF ABBREVIATIONS.

The word "bleach" is used for bleaching powder, and the term "bleach 35 per cent" designates bleaching powder containing 35 per cent. available chlorine.

The word "alcohol" designates ethyl alcohol and the term "alcohol 94 per cent." designates alcohol containing 94 per cent. CH_3CH_2OH by volume or 188 proof.

The atomic weights used in the calculations are rounded off to the nearest half unit, *viz.*: C = 12; Ca = 40; Cl = 35.5; H = 1; O = 16.

In some instances, particularly in warm weather, the reaction would start spontaneously, which could be observed by the stills warming up. In most cases, however, it was necessary to start the reaction the next morning by admitting steam direct to the stills. Care was taken to admit steam very gradually, otherwise the reaction would become very violent and the contents of the stills would boil over. The reaction having taken place, more steam was admitted, until all of the chloroform was distilled over. The distillation was continued until the distillate did not taste of alcohol or chloroform. The distillate coming after the chloroform (5 to 10 gallons) would be added to the next charge in the stills, and would be counted as alcohol, its alcoholic content being ascertained by the hydrometer. The chloroform was separated from the distillate and purified as described later on.

When I took charge of the plant, I conducted a series of operations in the same manner as they had been conducted for years, making the following observations:

I. 934 lbs. bleach, 35.8 per cent.; enough water to make 25 cu. ft.; 7.7 gallons alcohol, 94 per cent., were charged into still *B* at 5.0 P.M., the charge occupying less than 1 ft. in the 8-ft. still. The reaction commenced at 10 P.M., slow distillation taking place from 10 P.M. to 12.30 A.M. the following day. At 7 A.M. steam was admitted gradually, and 63 lbs. of crude chloroform of 1.40 specific gravity were distilled off. 50 cc. of this crude chloroform, shaken with 50 cc. water, left 44 cc. washed chloroform of 1.48 sp. gr. The total product of 63 lbs. crude chloroform made 58.6 lbs. of 1.48 sp. gr., after washing with water; 0.4 gallon alcohol, 94 per cent., was recovered in the after-distillate, and 0.7 gallon alcohol, 94 per cent., was recovered from crude chloroform by washing with water.

II. 971 lbs. bleach, 33.0 per cent., enough water to make 25 cu. ft., 6.9 gallons alcohol, 94 per cent., were charged into still *B* at 5 P.M. The reaction began at midnight, continued to 3 A.M., and 61 lbs. crude chloroform of 1.46 sp. gr. were withdrawn from the receiver the next morning; 50 cc. crude chloroform, 1.46 sp. gr., shaken with 50 cc. water, made 47 cc. washed chloroform, 1.48 sp. gr., and the 61 lbs. crude chloroform made 58.5 lbs. washed chloroform, 1.48 sp. gr.; 0.3 gallon alcohol, 94 per cent., was recovered in the after-distillate, and 0.4 gallon alcohol, 94 per cent., was obtained from the crude chloroform by washing with water.

III. 988 lbs. bleach, 33.7 per cent., enough water to make 25 cu. ft., 7.1 gallons alcohol, 94 per cent., were charged into still *B* at 5 P.M. The reaction did not commence during the night. Upon admitting steam slowly the next morning, the reaction commenced suddenly and the contents of the apparatus boiled over; 53.5 lbs. crude chloroform of 1.46 sp. gr. were obtained; 50 cc. of this chloroform, shaken with 50 cc. water, made 47 cc. washed chloroform, 1.48 sp. gr., and the 53.5 lbs. crude chloroform made 51.3 lbs. washed chloroform of 1.48 sp. gr.; 0.6 gallon alcohol, 94 per cent., was recovered in the after-distillate and 0.4 gallon alcohol, 94 per cent., was recovered from the crude chloroform by washing with water. The residue remaining in still *B* after the distillation contained some free chlorine or its equivalent.

IV. 959 lbs. bleach, 33.2 per cent., enough water to make 25 cu. ft., 7.0 gallons alcohol, 94 per cent., charged into still *B* at 6 P.M., commenced distilling voluntarily at 10.30 P.M., and continued distilling for 2½ hours. The distillation was finished the next morning by direct steam, making 66.5 lbs. crude chloroform, 1.45 sp. gr., 50 cc. of which shaken with 50 cc. water, made 46 cc. washed chloroform of 1.48 sp. gr. and the 66.5 lbs. crude chloroform made 62.6 lbs. washed chloroform, 1.48 sp. gr.; 0.4 gallon of alcohol, 94 per cent., was recovered in the after-distillate, and 0.6 gallon alcohol, 94 per cent., was recovered from the crude chloroform, by washing with water.

The mean temperature of the room at the time these experiments were made, was 16° C.

The alcohol contained in the after-distillate and in the wash water from crude chloroform was measured by specific gravity. This was not quite correct on account of the aldehyde and organic chlorine compounds, but it was the best that could be done under the circumstances.

1000 cc. after-distillate, 0.98 sp. gr., was distilled with 30 grams hydrated lime until 300 cc. were in the receiver; 2.3 cc. chloroform was separated. The distillate had a specific gravity of 0.930.

Each of the experiments, I to IV, constituted one day's work for one large apparatus, sketched in Fig. 1.

Conclusions and Observations from Experiments I to IV.—Summarizing the four experiments, 3825 lbs. bleach, averaging 33.9 per cent., equal to 3732 lbs., 35 per cent., enough water to make 100 cu. ft., 24.9 gallons alcohol, 94 per cent., made 231 lbs. chloroform crude washed by water, having a specific gravity of 1.48. The crude chloroform, upon washing with sulphuric acid, and redistilling, would lose 2.35 per cent. of its weight and would make 225.5 lbs. pure chloroform; 28.7 gallons alcohol, 94 per cent., was used and alcohol equivalent to 3.8 gallons alcohol, 94 per cent., was recovered from the after-distillate and from the wash water of the crude chloroform

The manufacture of 100 lbs. pure chloroform required, on an average, 1655 lbs. bleach, 35 per cent., and 11.05 gallons alcohol, 94 per cent.

The cost price of the materials in St. Louis, January, 1883, being $1.32 per 100 lbs. bleach, containing 35 per cent. chlorine, and $2.14 for one U. S. gallon of alcohol, 94 per cent., or 188 proof, the values of materials contributed to the cost of 100 lbs. pure chloroform, as follows:

1655 lbs. bleach, 35 per cent., at $1.32	$21.85
11.05 gallons alcohol, 94 per cent., at $2.14	23.65
Total	45.50

The yield of chloroform was much greater when the reaction started spontaneously, as in Expts. I, II and IV, than when it had to be started by admitting direct steam as in Expt. III. A particularly poor yield was obtained if the reaction was so violent that boiling over of the contents of the apparatus would occur.

In spite of the fact that only one-eighth of the space in the still was occupied by the charge, boiling over could not always be avoided.

In case the reaction was violent, the charge boiling over as in Expt. III, the values of the material would contribute to the cost of 100 lbs. pure chloroform, as follows:

1898 lbs. bleach, 35 per cent., at $1.32	$25.05
12.2 gallons alcohol, 94 per cent., at $2.14	26.11
Total	$51.16

In case the reaction started spontaneously, requiring 2 to 3 hours for its completion, as in Expt. I, II and IV, the average value of the materials would contribute to the cost of 100 lbs. of pure chloroform, as follows:

1584 lbs. bleach, 35 per cent., at $1.32	$20.91
10.71 gallons alcohol, 94 per cent., at $2.14	22.92
Total	$43.83

For the purpose of ascertaining the influence of *time* upon the *yield* of chloroform, the following experiments were made with the same apparatus:

V. 900 lbs. bleach, 35 per cent., enough water to make 25 cu. ft., 7.2 gallons alcohol, 94 per cent. The distillation was induced so as to begin 1½ hours after charging and was finished in 2 hours; 60.5 lbs. crude chloroform, 1.30 sp. gr., were obtained, which made 52.3 lbs. of washed chloroform, corresponding to 51 lbs. pure chloroform.

VI. 900 lbs. bleach, 35 per cent., enough water to make 25 cu. ft., 7.2 gallons alcohol, 94 per cent. The distillation was induced so as to begin 2 hours after charging and was finished in 2 hours; 62 lbs. crude chloroform, 1.32 sp. gr., were obtained, which made 50.1 lbs. washed, corresponding to 49.0 lbs. pure chloroform.

VII. 900 lbs. bleach, 35 per cent., enough water to make 25 cu. ft., 7.2 gallons alcohol, 94 per cent. Distillation was induced so as to begin 4 hours after charging and was finished in 3 hours; 61.8 lbs. crude chloroform, 1.41 sp. gr., were obtained which made 57.1 lbs. washed, corresponding to 55.8 lbs. pure chloroform.

VIII. 900 lbs. bleach, 35 per cent., enough water to make 25 cu. ft., 7.2 gallons alcohol, 94 per cent. Distillation was induced so as to begin 9 hours after charging, and was finished after 5 hours; 57.8 lbs. crude chloroform, 1.425 sp. gr., were obtained, which made 54.2 lbs. washed, corresponding to 53 lbs. pure chloroform.

Conclusions and Observations from Experiments V to VIII.—Delaying the distillation for four or more hours after the charge is made, tends to increase the yield of chloroform.

In each of the experiments (V to VIII), the residue in the still did not contain any large amount of active chlorine or its equivalent.

In each of the experiments an equivalent of 0.4 to 0.6 gallon of alcohol, 94 per cent., was recovered from the water distilling with the chloroform, and approximately 0.5 gallon of alcohol, 94 per cent., was recovered from the crude chloroform by washing with water. The same observation was made in Expts. I to IV.

The water coming over with the chloroform did not give any reaction for chlorine with silver nitrate but contained some organic chlorine compounds, which, upon distillation with lime, made chloroform. In one experiment, 1000 cc. distillate, mixed with 30 grams hydrated lime, and subjected to distillation in a glass retort, yielded 3.5 grams chloroform. The residue, which remained in the retort after this distillation, showed a strong reaction for chlorine with silver nitrate.

Five liters of watery distillate from the chloroform stills, upon fractional distillation, made about 4 cc. of an impure dichloraldehyde, boiling at 88° to 90° C.

The bleaching powder used for all these experiments contained an average of 15 per cent. of free hydrate of lime.

It was thought that possibly *an addition of hydrate of lime* might have an influence on the yield of chloroform, and with this in view, the following experiments were carried out:

IX. 900 lbs. bleach, 35 per cent., 150 lbs. hydrate of lime, enough water to make 25 cu. ft., 7.2 gallons alcohol, 94 per cent. The distillation was induced so as to begin 3 hours after charging, and was finished in 2½ hours; 62.25 lbs. crude chloroform, 1.36 sp. gr., were obtained, which made 47.7 lbs. washed, corresponding to 56.4 lbs. pure chloroform.

X. 900 lbs. bleach, 35 per cent., 170 lbs. hydrate of lime, enough water to make 25 cu. ft., 7.2 gallons alcohol, 94 per cent. The distillation was induced so as to begin 5½ hours after charging and was finished in 3½ hours; 70.25 lbs. crude chloroform, 1.36 sp. gr., were obtained, which made 62.6 lbs. washed, corresponding to 61.1 lbs. pure chloroform.

Conclusions from Experiments IX and X.—Comparing Expt. IX with Expt. VII, it would seem that the addition of hydrate of lime has no influence on the yield of chloroform if the distillation is induced about 3 hours after charging.

Comparing Expt. X with Expts. VIII and IX, it appears that the addition of hydrate of lime increased the output considerably, if at the same time the reaction is delayed to about 6 hours after charging.

The following table gives the materials used for 8 large lots, and the yields obtained from same, the work being conducted on the lines given in Expts. I to IV. In each operation, the after-distillate and wash water coming from the crude chloroform of the previous operation was added to the following charge. The alcohol contained therein is not given

in the table and only the *fresh* alcohol is given which was used in the operations:

TABLE I.

	Bleaching powder used.				100 lbs. bleach made	For 100 lbs. chloroform were used:	
Lot No.	Tons of 2000 lbs.	Per cent. Cl.	Alcohol, 94 per cent., used U. S. gal.	Chloroform, pure, obtained. Lbs.	chloroform. Lbs.	Bleach. Lbs.	Alcohol, 94 per cent. U. S. gal.
1	57	....	905	7934	6.96	1437	11.4
2	112	....	1768	15545	6.94	1441	11.37
3	60	....	926	7680	6.40	1562	12.06
4	63	28	924	6678	5.3	1887	13.83
5	233	....	3558	29358	6.3	1587	12.12
6	91	....	1426	13104	7.2	1389	10.88
7	87	35	1382	11966	6.87	1456	11.55
8	54	35½	870	7992	7.4	1351	10.88
Total....	757	....	11759	100257	....	....	.....
Average....		33⅓	....	.....	6.622	1510	11.73

100 lbs. chloroform required the following amounts of raw material:

	Lbs.
Bleaching powder, 33⅓ per cent.	1510
Alcohol, 100 per cent.	72–73

equal to 11.73 U. S. gallons, 94 per cent.

It is generally assumed that the formation of chloroform takes place according to the following reaction:

$$2[CH_3CH_2OH + 4CaClOCl] =$$
$$2CCl_3COH + 3Ca(OH)_2 + 5CaCl_2 + 2H_2O =$$
$$2CCl_3H + (HCOO)_2Ca + 2Ca(OH)_2 + 5CaCl_2 + 2H_2O$$

If this equation is correct, then for 100 lbs. chloroform the following quantities of raw materials should have been used:

	Lbs.
Bleach, 33⅓ per cent.	713.00
Alcohol, 100 per cent.	38.50

In place of this, more than twice as much bleach and almost twice as much alcohol were used in the manufacture of a lot of approximately 100,000 lbs. of chloroform.

Since the waste liquor from the stills contained only traces, but not any appreciable amounts of active chlorine, the waste of material could not be caused only by the oxidation of the formate of calcium to carbonate of calcium, or by the oxidation of alcohol, or by both.

If all of the formate of calcium coming from the chloroform reaction had been oxidized, then 178 lbs. bleach, 33⅓ per cent., would have been sufficient to do this work. By the formula

$$Ca(COOH)_2 + 2CaClOCl + Ca(OH)_2 =$$
$$2CaCO_3 + 2CaCl_2 + 2H_2O,$$

and the hydrated lime necessary for this reaction would also be furnished by the chloroform reaction.

But frequent analyses of the waste liquor have revealed the fact that only about ⁴/₅ of the formate of calcium formed in the reaction was oxidized, when ¹/₅ would run off with the waste liquor. This would leave more than 619 lbs. bleach, 33½ per cent., not accounted for, which, together with 33.5 lbs. alcohol, 100 per cent., were lost in the reaction.

This bleaching powder must have reacted with the alcohol, and the oxidation of part of the alcohol must have progressed to the formation of carbonic acid and water, since only in this way can the large quantities of carbonate of lime be accounted for, which were found in the waste liquors. A small proportion was consumed in the formation of dichloraldehyde, which was found in the water distilling with and after the chloroform, and another part formed, with alcohol, aldehyde and other products of decomposition, which had to be eliminated from the crude chloroform by washing with concentrated sulphuric acid, forming a black and often muddy mixture

The presence of organic chlorine compounds was also proven by the voluminous escape of pungent gases, which often drove the laborers from the apparatus room, making the work very disagreeable and difficult to control.

Expts. I to IV and also V to X were made with fresh alcohol, no alcohol coming from a previous operation being used.

In continuous operation the weak alcohol distilling off with the chloroform and the wash water from the crude chloroform of a previous operation was used in the following operation, and it was observed that in any first operation the yield of chloroform would be smaller than in subsequent operations in which the after-distillate and the wash water from crude chloroform containing alcohol and organic chlorine compounds were used in place of part of the alcohol.

If in the first operation the yield of chloroform was 5.5 per cent. from the weight of bleach, 35 per cent., used, then in the subsequent operations, in which the after-distillate and wash water from the previous operation were used in place of part of the alcohol, the charge would yield as much as 6.5 or even 7 lbs. chloroform from every 100 lbs. bleach, 35 per cent., used in the operation. This would seem to indicate that the alcohol is transformed into chloroform by steps or by a number of consecutive reactions. This being the case, it seemed not to be sufficient to draw conclusions from a single experiment, but a series of experiments had to be made, the after-distillate and wash water from the previous experiment always being used for the following experiments of the series.

It was also observed that the proportion of the yield from a first operation to the yield in a subsequent operation was fairly constant and for this reason Expts. I to X have comparative value.

The purification of the crude chloroform was accomplished by repeated washing with sulphuric acid, 66° B., to eliminate organic substances, and subsequent washing with a diluted solution of carbonate of sodium, followed by washing with water and final distillation in a rectifying still. The washing was done by hand. The finished chloroform was dried by shaking with dry chloride of calcium which was absolutely neutral, whereupon it was filtered and mixed with 1 per cent. absolute alcohol to improve its keeping qualities. It is essential that alcohol used for this purpose be almost free from water, and no alcohol having more than 0.2 per cent. water should be taken for this purpose.

The labor connected with the operation of six chloroform stills was as follows:

One foreman who operated six stills, two laborers for charging stills, one laborer for washing chloroform, $^1/_3$ the time of one operator for the rectifying still. Work was done in daytime only and 10 hours constituted a day's work. Approximately $^3/_4$ ton steam of 80 lbs. pressure was used for one operation in each still and six apparatus were operated once a day and each apparatus would take about 900 lbs. bleaching powder, making approximately 60 lbs. of chloroform.

The chloroform, when finished by rectification and dried by chloride of calcium, would be tested rigorously by two tests.

1. One ounce chloroform shaken with ½ ounce distilled water, upon addition of a few drops of a 10 per cent. solution nitrate silver, was not to give the faintest reaction for chlorine.

2. One ounce of chloroform, shaken for two minutes with $^1/_4$ ounce of colorless and pure sulphuric acid, 66° B., was not to show even the faintest decoloration, after standing ten minutes.

The process as described was at that time in use in many places for the production of chloroform. The results were not particularly bad, compared with those obtained by others. Inquiries from friends in the United States and in Europe, who were in a position to know, proved that other manufacturers obtained similar results. Besides, the fact that a number of manufacturers were eager to obtain possession of an improved process, when it was found, gave cause to believe that they themselves were working with inferior results.

The great losses in material seemed to me to justify the following investigation with reasonable prospect of success. There were two ways of going at it. One was to experiment with the large apparatus by changing conditions as far as the construction of the apparatus would permit. This method could be carried out in the regular course of work and the cost of experimenting would apparently be absorbed by current manufacturing expenses, but this course seemed to involve a deception of my employer and it seemed tedious and incomplete, since the arrangement of a given apparatus would not allow any fundamental changes, which might be necessary before results could be obtained.

The second way was to translate the process into small proportions and to carry the investigation out on a laboratory scale and to use the results of this investigation for improving the process on a larger scale.

There was a special consideration for me, which prompted me to choose the second method. I had entered the plant 3 years before I decided upon this investigation. Coming fresh from a German university, where I had graduated after 3½ years' study, and where I had held a position as assistant in charge of analytical work for 5 years following my graduation, I had no experience in the line of work which was entrusted to me, except what was given to me in the way of meager information by my employer.

The business in which I was employed ran entirely satisfactorily, with the process in use. The selling price of chloroform had been as high as $1.30, but had dropped to 90 cents, while its cost with the old process was about 50 cents per lb.

My employer had picked up this process in a German factory, where it had been operated for a long time, and he thought he was operating the most practical process known to successful manufacturers. In this assumption he did not seem to be mistaken, since inquiries subsequently made established the fact that other German manufacturers operated at a similar disadvantage.

There was little inclination to spend money for experiments and I did not think it advisable to make radical changes with the larger apparatus in the regular routine of business where expenses for experimental work were absorbed by current manufacturing expenses, upon my own responsibility. This was particularly the case, since experiments were to be made in a direction in which German manufacturers were known to have experimented, but had failed.

By day my time was taken up with routine work, and if I wanted to make the research, I had to do it at night. A rather primitive laboratory, consisting of a room in the basement with an experimenting table was at my disposal and I had gas for lighting and heating. Water was to be carried in with buckets. Whatever apparatus I needed I secured at my own expense, since it was my intention to remain the owner of the improved process, if I should find it. Bleaching powder, alcohol and reagents I used from the stock of the company, but I kept account of whatever I used for the purpose of settling for it as soon as I could offer an improved process to my employer.

The work was designed in the following manner:

1. The existing manufacturing process was translated into laboratory scale by carrying out the operation in glass apparatus, but taking the same proportions of materials as were used in the large stills and working them in apparatus of proportionate dimensions. The results obtained on a small scale were compared with the results in the large plant, and a constant was obtained which allowed me to compare the results on a small scale made with an apparatus of definite design, with results which could be expected in actual practice with larger stills.

2. With the apparatus arranged as described in the first paragraph, the proportions of materials and conditions of operations were varied, care being taken to change the apparatus itself as little as possible, since any change in the small apparatus would imply a corresponding change in the large plant. In this manner the expenses connected with such changes were kept down to the least possible amount.

3. The process arrived at by the research was translated into practice by changing the large apparatus by the results of the experiments, and using the proportions of materials and temperatures found to be most profitable in the research work.

The translation of the existing manufacturing process to a laboratory scale was done by arranging the glass apparatus Fig. 2, and by executing with this apparatus the experiments, series *A* and *B*, for

the purpose of determining the relation between the results obtained by operations on a factory and laboratory scale

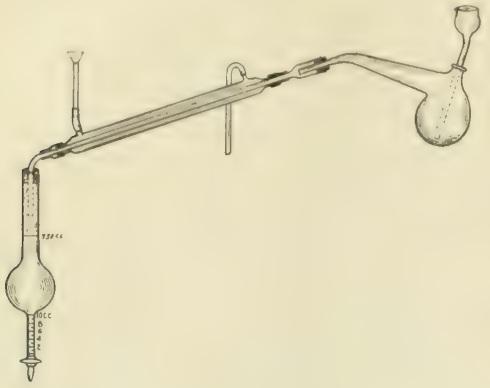


Fig. 2.

Experiments, Series A, comprising two experiments, and representing two days' work in the plant, were made for the purpose of comparing factory results with laboratory experiments. Apparatus Fig. 2 used, with 1500 cc. retort, measured inclusive of neck, and having a straight neck.

During the distillation, 2 cc. water were introduced into the retort by way of a long stem funnel for every 1 cc. water distilled, in order to imitate the accumulation of condensed water from direct steam in the large stills.

1. Materials used: 100 grams bleach, 35 per cent.; enough water to make 175 cc.; 6.7 cc. alcohol, 94 per cent.; mixed at 20° C. and distilled. Products obtained: 5.7 grams washed chloroform, sp. gr. 1.48.

2. Materials used: 100 grams bleach, 35 per cent.; enough water to make 175 cc.; 6.7 cc. alcohol, 94 per cent.; mixed at 20° C. and distilled. Products obtained: 5.5 grams washed chloroform, sp. gr. 1.48.

Conclusion.—Comparing the results of laboratory Expts. 1 and 2 of Series A, with factory Expts. V to VIII, it appears that experiments on a large scale yield somewhat more chloroform than laboratory experiments.

The results of laboratory experiments carried out in the manner described are of such character that conclusions can be drawn with reference to the working of corresponding experiments made on a large scale.

This is confirmed by later observations, comparing experiments made on a large and small scale, and the difference would seem to range from 5 to 7 per cent. of the product.

Compare Series B with the working of large lot 7, Table I.

Experiments, Series B, comprising ten experiments and representing ten days' work in the large plant, were made for the purpose of determining the yield in subsequent operations, if the after-distillate and wash water of crude chloroform from the previous experiment were used for the following operation, in a manner which imitated continuous work in actual practice.

The proportion of alcohol to bleach was regulated to be the same in the old process, lot No. 7, Table I, in which lot 87 tons = 78,926 kg. bleach, 35 per cent., with 1382 U. S. gallons = 5230 liters alcohol, 94 per cent., made 11,966 lbs. = 5428 kg. pure chloroform. For this reason this series of experiments, compared with lot 7, Table I, gives a good idea of the working of the process on a large and laboratory scale.

Apparatus Fig. 2 used, with 1500 cc. retort, having a straight neck.

During the distillation, 2 cc. water were introduced into the retort by way of the long stem funnel for every 1 cc. water distilled, in order to imitate the accumulation of condensed water from direct steam in the large stills.

1. Materials used: 100 grams bleach, 35 per cent.; enough water to make 175 cc.; 6.7 cc. alcohol, 94 per cent.; mixed at 20° C. and distilled. Products obtained: 5.5 grams chloroform washed, 1.48 sp. gr., 50 cc. diluted alcohol (distillate A).

2. Materials used: 100 grams bleach, 35 per cent.; 50 cc. distillate A; enough water to make 175 cc.; 6.7 cc. alcohol, 94 per cent.; mixed at 20° C. and distilled. Products obtained: 6.4 grams washed chloroform, 1.48 sp. gr., 50 cc. diluted alcohol (distillate B).

3. Materials used: 100 grams bleach, 35 per cent.; 50 cc. distillate B; enough water to make 175 cc.; 6.7 cc. alcohol, 94 per cent.; mixed at 20° C. and distilled. Products obtained: 6.9 grams washed chloroform, 1.48 sp. gr., 50 cc. diluted alcohol (distillate C).

The following members of this series were made in the same manner. In each number, bleach and water were well mixed, filled up to the required volume, and put cold into the retort of the apparatus. After-distillate, wash water of crude chloroform, and alcohol were added when cold; the reaction was induced by gently heating.

The results of experiments, Series B, are entered in the following table:

Table II.

	Material used.				Products.	
Series B. No.	Bleach, 35 per cent. Grams.	Water to make solution. cc.	Diluted alcohol from previous operation. cc.	Alcohol, 94 per cent. cc.	Washed chloroform, 1.48 sp. gr. Grams.	Diluted alcohol. cc.
1	100	175	..	6.7	5.5	50
2	100	125	50	6.7	6.4	50
3	100	125	50	6.7	6.9	50
4	100	125	50	6.7	6.8	50
5	100	125	50	6.7	7.0	50
6	100	125	50	6.7	6.9	50
7	100	125	50	6.7	6.8	50
8	100	125	50	6.7	7.1	50
9	100	125	50	6.7	6.9	50
10	100	125	50	6.7	6.8	50
Totals...	1000	...	..	67.0	67.1	.

The 67.1 grams washed chloroform, 1.48 sp. gr.,[1] corresponded to 65.5 grams of pure chloroform, 1.5 sp. gr., and the amount of chloroform obtained was approximately 1 gram of chloroform for every cubic centimeter alcohol, 94 per cent., used in the experiment.

Comparing the results of experiments, Series B, with the results obtained in lot 7, Table I, in which 78,926 kg. bleach, 35 per cent., and 5230 liters alcohol, 94 per cent., made 5428 kg. pure chloroform (which is equivalent to 7.042 grams washed chloroform, 1.48 sp. gr., from 6.626 cc. alcohol, 94 per cent., and 100 grams bleach, 35 per cent.), it is seen that the difference between results obtained in the labora-

[1] 100 grams washed chloroform, 1.48 sp. gr., would make 97.65 grams pure chloroform, after purifying with sulfuric acid, 66°, and redistilling.

tory and the results in the large plant was about 5 per cent. in favor of practical work for bleach, while for alcohol the consumption was not more than in actual work.

Conclusion.—The results obtained in the large apparatus in the plant and those obtained in the laboratory with apparatus Fig. 2 could be compared, the difference being about 5 per cent. in favor of work on a large scale for bleach.

For this reason reliable conclusions could be drawn from laboratory experiments made with apparatus Fig. 2, upon the working of the large apparatus in the plant.

In the following pages a line of experiments is recorded which led systematically to a superior process and by the results of these experiments the plant was reconstructed, doing, after a very simple change, twice the work which it did before, and making, at the same time, a saving of almost one-third of all the bleaching powder used in the process.

Experiments, Series C, comprising nine experiments and representing nine days' work in the plant, were made for the purpose of ascertaining whether dilution of the charge of water would have any influence upon the yield of chloroform.

Apparatus Fig. 2 was used with 1500 cc. retort. The experiments were made in the same manner as the experiments of series B, with the only exception that 1000 cc. water were taken in place of 175 less volume of 100 grams bleach dissolved in same, and that 300 cc. were distilled off instead of 50 cc.

TABLE III.

	Materials used.				Products.	
Series C. No	Bleach, 35 per cent. Grams.	Water. cc	After-distillate from previous portion. cc	Alcohol, 94 per cent. cc.	Washed chloroform. Grams.	After-distillate. cc
1	100	1000	..	6.7	none	300
2	100	700	300	6.7	trace	300
3	100	700	300	6.7	0.3	300
4	100	700	300	6.7	0.5	300
5	100	700	300	6.7	3.0	300
6	100	700	300	6.7	2.4	300
7	100	700	300	6.7	3.3	300
8	100	700	300	6.7	3.5	300
9	100	700	300	6.7	3.0	300

Conclusions from Series C Compared with Series B.—Dilution with water would diminish the yield of chloroform.

TABLE IV.

	Materials used.				Products.	
Series D No.	Bleach, 35 per cent. Grams.	Water. cc	After-distillate from previous portion. cc.	Alcohol, 94 per cent. cc.	Washed chloroform. Grams	After-distillate. cc.
1	100	1000	...	20	1.2	300
2	100	700	300	20	3.6	300
3	100	700	300	20	5.4	300
4	100	700	300	20	7.5	300
5	100	700	300	20	6.7	300
6	100	700	300	20	9.0	300
7	100	700	300	20	9.7	300
8	100	700	300	20	10.5	300
9	100	700	300	20	10.3	300
10	100	700	300	20	10.5	300
11	100	700	300	20	9.8	300
12	100	700	300	20	10.0	300

Experiments, Series D, comprising twelve experiments and representing twelve days' work in the plant, were made for the purpose of ascertaining whether dilution with water, combined with increase of alcohol, would have any influence upon the yield of chloroform.

Apparatus and operation were the same as in Series C.

Remarks.—The last after-distillate had a specific gravity of 0.970. The crude chloroform from Expts. 8 to 12 combined was washed with 50 cc. concentrated sulphuric acid, whereby its weight was reduced from 40 grams to 46 grams, the purified chloroform having a specific gravity of 1.5.

The sulphuric acid was very little discolored, much less so than by crude chloroform obtained in lot 7, Table I, thus showing greater purity of the crude product.

Conclusions from Series D.—Comparing Series C and D, it appears that the concentration of alcohol is of material interest upon the yield of chloroform. Taking from table, Series L, that 20 cc. alcohol make more than 16 grams chloroform, it follows from table, Series D, that in the eighth operation, in which the concentration of alcohol was nearly 10 per cent., the maximum yield was reached. Greater concentration did not give any further increase in the output of chloroform.

Comparison of Series D with Series B shows an increase of the alcohol proportion in presence of more water; increases the yield of chloroform obtained by the old process.

The chloroform obtained is purer than by the old process.

Experiments, Series E, comprising four experiments, were made to determine whether a large excess of alcohol will increase the yield of chloroform.

Apparatus Fig. 2 used, with 1500 cc. retort. In each of the experiments, 700 cc. alcohol and water were distilled off, after the chloroform and the alcoholic distillate from each operation was used for the following operation, in place of alcohol, no fresh alcohol being added.

1. Materials used: 100 grams bleach, 35 per cent.; enough water to make 500 cc.; 500 cc. alcohol, 94 per cent.; mixed at 20° C. and distilled. Products obtained: 6.7 grams washed chloroform, sp. gr. 1.48, 700 cc. diluted alcohol (distillate A).

2. Materials used: 100 grams bleach, 35 per cent.; enough water to make 300 cc.; 700 cc. distillate A; mixed at 20° C. and distilled. Products obtained: 9.0 grams washed chloroform, sp. gr. 1.48; 700 cc. diluted alcohol (distillate B).

3. Materials used: 100 grams bleach, 35 per cent.; enough water to make 300 cc.; 700 cc. distillate B; mixed at 20° C. and distilled. Products obtained: 11.5 grams washed chloroform, sp. gr. 1.48; 700 cc. diluted alcohol (distillate C).

4. Materials used: 100 grams bleach, 35 per cent.; enough water to make 300 cc.; 700 cc. distillate C; mixed at 20° C. and distilled. Products obtained: 9.1 grams washed chloroform, 1.48 sp. gr.; 700 cc. diluted alcohol (distillate D).

TABLE V.—COMPARISON OF EXPERIMENTS, SERIES C, D AND E.

		Chloroform washed, sp. gr 1.48, obtained in		
Experiment No.	Bleach, 35 per cent. used. Grams.	Series C. Grams.	Series D. Grams.	Series E. Grams.
1	100	none	1.2	6.7
2	100	trace	3.6	9.0
3	100	0.3	5.4	11.5
4	100	0.5	7.5	9.1
5	100	3.0	6.7	
6	100	2.4	9.0	
7	100	3.3	9.7	
8	100	3.5	10.5	

Experiments, Series E^a, comprising four experiments, and representing four days' work in the plant, were made for the same purpose as E. Only 200 cc. alcohol added in the first operation, in place of 500 cc.

Apparatus Fig. 2 used, with 1500 cc. retort.

1. Materials used: 100 grams bleach, 35 per cent.; enough water to make 800 cc.; 200 cc. alcohol, 94 per cent.; mixed at 20° C. and distilled. Products obtained: 6.75 grams washed chloroform, sp. gr. 1.48; 700 cc. diluted alcohol (distillate A).

2. Materials used: 100 grams bleach, 35 per cent.; enough water to make 300 cc.; 700 cc. distillate A; mixed at 20° C. and distilled. Products obtained: 8.4 grams washed chloroform, sp. gr. 1.48; 700 cc. diluted alcohol (distillate B).

3. Materials used: 100 grams bleach, 35 per cent.; enough water to make 300 cc.; 700 cc. distillate B; mixed at 20° C. and distilled. Products obtained: 10.5 grams washed chloroform, sp. gr. 1.48; 700 cc. diluted alcohol (distillate C).

4. Materials used: 100 grams bleach, 35 per cent.; enough water to make 300 cc.; 700 cc. distillate C; mixed at 20° C. and distilled. Products obtained: 10.9 grams washed chloroform, sp. gr. 1.48; 700 cc. diluted alcohol (distillate D).

Experiments, Series E^b, comprising four experiments and representing four days' work in the plant, were made for the same purpose as E. Only 100 cc. alcohol were added in the first operation in place of 500 cc.

Apparatus Fig. 2 used, with 1500 cc. retort. Operations the same as E, only 500 cc. diluted alcohol distilled off, in place of 700 cc.

1. Material used: 100 grams bleach, 35 per cent.; enough water to make 900 cc.; 100 cc. alcohol; mixed at 20° C. and distilled. Products obtained: 6.7 grams chloroform washed, 1.48 sp. gr.; 500 cc. diluted alcohol (distillate A).

2. Materials used: 100 grams bleach, 35 per cent.; enough water to make 500 cc.; 500 cc. distillate A; mixed at 20° C. and distilled. Products obtained: 8.2 grams washed chloroform, sp. gr. 1.48; 500 cc. diluted alcohol (distillate B).

3. Materials used: 100 grams bleach, 35 per cent.; enough water to make 500 cc.; 500 cc. distillate B; mixed at 20° C. and distilled. Products obtained: 7.5 grams washed chloroform, sp. gr. 1.48; 500 cc. diluted alcohol (distillate C).

4. Materials used: 100 grams bleach, 35 per cent.; enough water to make 500 cc.; 500 cc. distillate C; mixed at 20° C. and distilled. Products obtained: 6.7 grams washed chloroform, sp. gr. 1.48; 500 cc. diluted alcohol (distillate D).

Conclusions from Series E, E^a and E^b.—The presence of large excess of alcohol increases the yield of chloroform from the same amount of bleach, 35 per cent., but the increase is not in proportion to the amount of alcohol present. Series E^b indicates that 100 cc. alcohol, 94 per cent., for 100 grams bleach and enough water to make 1000 cc., give the largest yield in chloroform, with the least amount of alcohol. The yield was diminished in the third and fourth operations of Series E^b, when about 15 cc. of the 100 cc. alcohol were consumed for the production of 6.7 and 8.2 grams = 14.9 grams chloroform obtained in operations 1 and 2.

Increase of the alcohol proportion to 200 cc. and even to 500 cc. for 100 grams bleach, 35 per cent., and enough water to make 1000 cc., does not increase the yield of chloroform.

TABLE VI.—COMPARING RESULTS OF SERIES E, E^a AND E^b.

Operations. No.	Series E. 100 grams bleach, 35 per cent., 500 cc. alcohol, 94 per cent., water to make 1000 cc. Temp. of mixing, 20° C. Made washed chloroform. Grams.	Series E^a. 100 grams bleach, 35 per cent, 200 cc. alcohol, 94 per cent., water to make 1000 cc. Temp. of mixing, 20° C. Made washed chloroform. Grams.	Series E^b. 100 grams bleach, 35 per cent., 100 cc. alcohol, 94 per cent., water to make 1000 cc. Temp. of mixing, 20° C. Made washed chloroform. Grams.
1	6.7	6.75	6.7
2	9.0	8.4	8.2
3	11.5	10.5	7.5
4	9.1	10.9	6.7

(*To be concluded.*)

THE CAUSES FOR VARIATIONS IN VOLATILE MATTER DETERMINATIONS.[1]

By S. W. PARR.

Received January 1, 1912.

While the method for the determination of volatile matter in coal must doubtless remain empirical in character, it is evident that concordant results can come only from a procedure which is based upon a knowledge of the relative influence of the various factors that enter into the process. It seems probable that essentially all of the variations may be referred to one or more of the following conditions:

(*a*) Mechanical loss;
(*b*) Oxidation under the cover;
(*c*) Variation in the discharge of hydrogen in the latter part of the process;
(*d*) The speed of decomposition in the early carbonization of the coal.

It is the purpose of this note to indicate that the variations under (*a*), (*b*) and (*c*) are small in amount and easily controlled or eliminated, and that practically all of the variation centers in (*d*) and depends upon the speed with which the heavier or richer volatile constituents are discharged from the mass.

(*a*) *Mechanical Loss.*—The difficulty of mechanical loss has already been discussed in a former paper.[2]

Further experience in the use of a small amount of kerosene as therein recommended is confirmatory of the advantage of that procedure as a means for lessening the mechanical loss and promoting uniformity of results.

(*b*) *Oxidation under the Cover.*—It seems evident that the ordinary flat cover to a platinum crucible, no matter how well fitting so far as the eye can determine, is nevertheless responsible for many irregularities, possibly due to slight displacement of the cover at the time of greatest evolution of gases. To guard against this difficulty, the suggestion of Shimer[3] has been used, namely, providing a small platinum capsule with rather light flexible sides which would fit into the main crucible and adjust itself to the irregularities of the same, thus providing a good fit without the overhanging feature of the flat cover with its tendency to promote air currents in and out of the crucible. That this device is a positive help towards uniformity is shown from the following table. The samples were given identical treatment as to heat and time. Fifteen drops of kerosene were

[1] Coal studies, in connection with the work of the Illinois State Geological Survey.

[2] THIS JOURNAL, December, 1911.

[3] *Ibid.*, **1**, 518 (1909).

used in both series to eliminate variables due to mechanical loss, the only difference being the use of an inserted capsule as a cover in one case, Series B, and a regular flat, well-fitting cover in the other, Series A:

TABLE I.—SUMMARY OF THIRTEEN RESULTS

	A.	B.
Extreme of variation in duplicates	0.39%	0.21%
Number of duplicates having variations from the average less than 0.1 per cent	4	10
Average of total variations	0.16%	0.07%

(*c*) *Residual Hydrogen.*—The extent to which the residual volatile matter, mainly hydrogen, is driven off, is a possible source of variation, but the variable is easy of control. A study of the work of Porter and Ovitz,[1] and also of Burgess and Wheeler,[2] shows that the discharge of hydrogen is quite uniform for a given temperature, and that with bituminous coal the volatile matter as represented by this element is given off much more rapidly below 900° than above that temperature; so that if a temperature above 900° is maintained within reasonable limits the variation in the indicated volatile matter will be small.

At temperatures of 1050° or 1100° the discharge of this constituent is so nearly complete that very close check results should be expected. At a temperature approximating 950° the results should still check with themselves, but the indicated volatile matter would be less than with the higher temperatures. The ratio of difference would doubtless vary slightly with different coals. The conditions thus indicated call for a uniform heat which may be maintained at a reasonably uniform temperature and above 900°. Whether it shall be arbitrarily placed near the lower limit, say 950°, with an incomplete discharge of the volatile matter, or near the upper practicable limit, say 1100°, with a more nearly complete discharge of volatile, it is not the purpose here to decide. It is desired now only to show how closely the above proposition is confirmed by the data at hand.

A number of coals were tested in duplicate under identical conditions as to (*a*) use of kerosene, and (*b*) capsule cover. The heat applied for Series A was 950° to 980° throughout, as obtained by use of a Méker burner. In Series B the same heat from the same burner was applied for two minutes. The crucible was then subjected for five minutes to a temperature of 1100°. They indicate that by eliminating all other variables, the completeness of the hydrogen discharge for a given temperature is very definite, increasing noticeably in exactness with the higher temperatures and the more complete discharge of the hydrogen. So far as these results go, at least, they furnish a striking verification of the above proposition concerning the hydrogen variable.

In order to determine whether lower temperature for the first two minutes of heating would be neutralized in its effect by the subsequent increase for five minutes to 1100°, a number of the coals in Table II were subjected to a much lower temperature, approx-

[1] Bull. **1**, U. S. Bureau of Mines, "The Volatile Matter of Coal," 1910.

[2] *Journal Chem. Soc. (London)*, **97**, 1917 "The Volatile Constituents of Coal. 1910."

TABLE II. COMPARISON OF DUPLICATES USING DIFFERENT TEMPERATURES FOR LAST PART OF PROCESS.

Lab. No.	Kind of coal.	7 min. at 950°. Per cent.	Variation + or − from average. Per cent.	2 min. at 950°. 5 min. at 1100°. Per cent.	Variation + or − from average. Per cent.
4513	Fulton Co.	42.01		42.80	
		41.85		42.77	
		41.93	0.08	42.78	0.02
4516	Sangamon Co.	39.70		40.71	
		39.73		40.70	
		39.71	0.02	40.70	0.01
4517	"	39.60		41.10	
		40.03		41.06	
		39.81	0.22	41.08	0.02
4518	"	37.37		38.91	
		37.33		38.88	
		37.35	0.02	38.90	0.02
4519	"	38.81		40.16	
		38.78		40.19	
		38.80	0.02	40.18	0.02
4520	"	40.09		41.13	
		40.37		41.10	
		40.23	0.14	41.12	0.02
4521	"	39.61		40.98	
		39.82		41.02	
		39.71	0.11	41.00	0.02
4522	"	40.31		41.44	
		40.27		41.44	
		40.29	0.02	41.44	0.00
4523	Logan Co.	40.41		40.94	
		40.36		40.91	
		40.38	0.03	40.93	0.02
4524	"	39.27		40.21	
		38.98		40.21	
		39.12	0.15	40.21	0.00
	Average of variations,		0.08		0.015

TABLE III.—SHOWING THE EFFECT ON VOLATILE MATTER OF DIFFERENT TEMPERATURES FOR THE FIRST TWO MINUTES OF HEATING.

Lab. No.	Kind of coal.	2 min. at 950°. 5 min. at 1100°.	2 min. at 600°. 5 min. at 1100°.	Difference in average values.
4519	Sangamon Co., Ill.	40.16	38.91	
		40.19	38.86	
		40.18	38.89	−1.29
4520	"	41.13	39.45	
		41.10	39.77	
		41.12	39.61	−1.51
4521	"	40.98	35.59	
		41.02	39.69	
		41.00	39.64	1.36
4522	"	41.44	40.10	
		41.44	39.97	
		41.44	40.03	−1.41
4523	Logan Co., Ill.	40.94	40.01	
		40.91	40.03	
		40.93	40.02	−0.91
			Average.	−1.30

imately 500° to 600°, or such that the time for driving off the heavy volatile material was noticeably prolonged, though still practically completed within the two minutes allowed in Table II. These results show that the lower temperatures cause a larger fixation of carbon and a consistently lower percentage of volatile matter, thus confirming the proposition as stated under (*d*) as to variations caused by the speed of the preliminary decomposition. Also by the close agreement of the duplicates there is added further confirmation to the proposition under (*c*) as to the constancy of the hydrogen discharge at a high temperature.

(*d*) *Carbonization Variables.*—Under (*d*) the variations which occur in the first part of the carbonization bear a direct relation to the speed with which that part of the process is carried out. It is true that a higher or lower temperature will influence the rapidity with which decomposition takes place, but this is by no means the only factor. For example, with the same crucible and the same temperature, a higher volatile discharge will be recorded if the mass of coal is spread with a concave surface so that more of the coal is brought into contact with the metal. Or to reverse the conditions, a small 10-gram crucible will have less superficial contact with the metal than a 30-gram crucible. If in each case the coal is allowed to assume its natural shape with level surface, the larger crucible will discharge the larger amount of volatile matter. Again the same 10-gram crucible will yield more volatile if the coal is spread around the sides, giving it a concave surface, and increasing the area exposed to the crucible. These four sets of conditions are illustrated in the following table:

TABLE IV.—SHOWING VARIATIONS DUE TO SPEED OF VOLATILIZATION.

Lab. No	Kind of coal.	A. 30-g. plat. cruc. coal with flat surface. Per cent.	B. 30-g. plat cruc. coal with concave surface. Per cent.	C. Compare B with A. Per cent.	D. 10-g. plat. cruc. coal with flat surface Per cent.	E. 10-g. plat. cruc. coal with concave surface. Per cent.	F. Compare E with D. Per cent.
4389	Bureau Co., Ill.	47.03	47.95	+0.92	45.82	46.48	+0.66
1889	Logan Co., Ill. . .	42.94	44.65	+1.71	42.29	43.21	+0.92
213	Lignite, N. D. .	56.93	57.18	+0.25	55.61	55.44	—0.17
2775	Rock Island Co., Ill . .	46.02	47.44	+1.42	45.02	45.56	+0.54
1810	Franklin Co., Ill .	38.39	38.72	+0.33	37.76	38.31	+0.55
2773	Anthracite. .	9.23	9.01	—0.18	8.58	8.67	+0.09
			Average,	+0.78			+0.43

It seems evident from the above data that the greatest source of variation resides in that part of the process which involves the distillation of the fat or heavy volatile portion of the coal. These variations also are due to seemingly small influences, as high as 1.7 per cent. in one instance, in sample No. 1889, Table IV, being due to the disposition of the charge against the sides of the crucible. If comparison were made as between the large and the small crucible as in column A and D, a variation of 1.21 per cent. is shown in sample 4389, due to this cause alone. It is evident, therefore, that in standardizing this part of the procedure, more than the simple matter of temperature must be taken into account.

Other evidence, all in the same direction has been obtained wherein a weighed amount of clean, ignited sea sand was mixed with the coal. This procedure gives a coke of uniform texture and obviates any tendency on the part of the coke to swell. But the yield of volatile matter is consistently lower, owing to the small retardation of the decomposition processes. Another bit of evidence in the same direction is the use of a porcelain crucible which, again retards the process and gives lower results by from one to two per cent. This reduction in yield with a porcelain crucible can be very largely counteracted by using a correspondingly higher temperature, but more data is necessary before a conclusion can be drawn as to the conditions wherein porcelain can be substituted for platinum.

Other influences, such as the presence or absence of free moisture, especially in lignites, the use of a muffle instead of a flame, etc., have been partially tested but not sufficiently to be reported upon at this time, further than to say that the Méker burner promises to afford a much more even temperature than the ordinary Bunsen burner; or rather, it delivers a large amount of heat instead of a small localized zone at the tip of a small flame. There is a decided advantage also in the larger volume of flame which more completely envelops the crucible and furnishes at the same time an atmosphere with but little oxidizing property.

It is not the purpose of this paper to make recommendations as to the best procedure since the whole matter is under consideration by the committee on revision of methods for coal analysis. It may be said, however, that the experiments indicate certain essentials, outlined as follows:

1. Definiteness of temperature.
2. The employment of a temperature not below 900° or 950°.
3. Use of a crucible of given size and shape.
4. A capsule cover fitting inside of the crucible and not on top.
5. The use of kerosene to moisten the charge.
6. If a burner is to be used, the Méker type has a great advantage in furnishing a larger volume of heat less localized than that of the ordinary Bunsen type.
7. A small crucible is preferable to a large one, as it is more readily enveloped completely by the flame of the burner and the coal mass is less subject to variations in form. This is very important in view of the large variables that may enter into the early stages of decomposition.

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MONEL METAL.

By RICHARD H. GAINES.

Received January 6, 1912.

HISTORY.

About seven years ago, one of the large smelting companies began investigating the chemical and physical properties of an alloy that had been reduced directly from a nickel-copper matte, without the

previous separation of the two metals. This alloy was found to possess not only the more valuable properties of nickel, but other desirable properties in addition, that would ensure a wide usefulness, and owing to the simple method of production, was obtainable at about one-third the cost of nickel. The alloy consists primarily of nickel and copper in the proportion of three parts of nickel to one part of copper, this being the proportion in which the two metals are found together in nature in the great deposits of nickel ore at Copper Cliff in Canada.

The old Swedish and German miners supposed the mineral küpfernickel to be a counterfeit or base ore of copper. A fuller knowledge of nickel led to its being better appreciated, and it is now worth nearly three times as much as copper.

Nickel and copper are associated in enormous pyrrhotite deposits in the Sudbury district of Ontario, Canada, and one of the most difficult problems in the treatment of these ores has been that of separating the two metals. In 1905–6, the International Nickel Company, considering, no doubt, that for many purposes there was no need to separate the amicable metals nickel and copper, took up the problem of reducing them together and obtaining an alloy of the two metals in the proportions in which they occur in the ore. The method adopted consists merely in eliminating the impurities, except a small percentage of reduced iron and a minor quantity of other substances which remain with the alloy.

PROCESS OF MANUFACTURE.

Synopsis.—The ore from the mines is first reduced to a matte, which is blown until the iron is nearly eliminated, the sulphur is removed by roasting, and the combined oxides remaining are reduced to metal.

The general method of production includes roasting the ore in heaps, followed by smelting in a blast furnace, and further enriching in a converter, which yields a high-grade matte containing about 80 per cent. nickel and copper, from 1–2 per cent. iron, and the rest sulphur. By careful attention to the furnace charge, it now is claimed that a Bessemer matte can be produced within 1 per cent. of the required proportion. The rich matte is shipped to the Orford refinery, where it is ground and roasted in hand rabbled reverberatory furnaces to remove the sulphur, carbonate of soda being used to finish the elimination of the sulphur. The product should be oxides of nickel and copper, with a small proportion of iron, and only a trace of sulphur. This is charged with charcoal into a reverberatory melting furnace fired with oil. The nickel and copper oxides are thus reduced to metal, and melted.

The alloy thus obtained was found to possess such valuable properties as would ensure it a very wide use on its own account. It was named Monel metal after Mr. Ambrose Monel, the president of the International Nickel Company.

COMPOSITION.

The ores of the Sudbury district vary both in the amount and proportion of nickel and copper, and, therefore, the proportions of these two metals in the alloy will vary within certain limits with the composition of the ore treated. The ore from which the Monel metal is derived contains generally about 4.85 per cent. of nickel to about 1.75 per cent. copper. When this ore, as it occurs in nature, is reduced to metal, the resulting alloy contains from 66–70 per cent. nickel, from 23–28 per cent. copper and from 3–5 per cent. of other metals, including iron, and a small proportion of manganese.

ANALYSES OF CAST MONEL METAL.
Samples taken at the foundry of the Bayonne Casting Co., Bayonne, N. J.
Per cent.

Lab. No.	Description.	Copper.	Carbon.	Iron.	Nickel.	Silicon.	Manganese.	Cobalt.	Total.
1146	Heat 301	26.59	0.27	3.19	68.22	1.10	0.26	Trace	99.63
1147	Heat 307	27.02	0.31	2.40	68.49	1.08	0.49	Trace	99.79
1148	Heat 308	26.59	0.43	2.87	68.23	1.24	0.44	Trace	99.80
1149	Heat 312	27.04	0.39	2.68	68.10	1.17	0.37	Trace	99.75
1150	Heat 315	27.27	0.39	2.40	68.50	1.23	0.09		99.88
1151	Heat 318	26.81	0.38	2.54	68.30	1.36	0.23		99.62
1152	Heat 329	27.53	0.31	2.16	68.28	1.41	0.14		99.83
1153	Heat 335	27.38	0.25	3.33	68.46	1.24	0.11		99.77

ANALYSES OF ROLLED MONEL METAL.
Samples taken at the foundry of the Bayonne Casting Co., Bayonne, N. J.
Per cent.

Lab. No.	Description.	Copper.	Carbon.	Iron.	Nickel.	Silicon.	Manganese.	Cobalt.	Total.
1154, No. 1	Test 275	26.57	0.28	2.09	69.04	0.16	1.32	Trace	99.46
1155, No. 2	Test 275	26.71	0.44	2.11	68.81	0.17	1.35	Trace	99.59
1156, No. 4	Test 275	26.99	0.37	2.07	68.89	0.18	1.26	Trace	99.76
1157, No. 6	Test 275	24.76	0.33	2.44	69.83	0.37	1.82	Trace	99.55
1158, No. 7	Test 275	26.94	0.39	2.16	68.48	0.12	1.54	Trace	99.63
1159, No. 8	Test 275	26.21	0.43	2.41	68.63	0.20	1.73	Trace	99.61

ANALYSES OF FORGED MONEL METAL.
Sample submitted by the Bayonne Casting Co., Apr. 6, 1911.
Per cent.

Lab. No.	Description.	Copper.	Nickel.	Manganese.	Iron.	Carbon.	Total
1021	Specimen taken midway between center and outside of billet	26.69	69.45	1.38	2.13	0.19	99.84
1022	Specimen from center of billet	26.78	69.52	1.50	2.14	0.17	100.11
1023	Specimen from outside of billet	26.83	69.54	1.48	2.19	0.18	100.22

C. F. Burgess and James Aston[1] give the following analysis of a sample of Monel metal examined in 1909:

	Per cent.
Nickel	67.96
Copper	26.00
Iron	2.80
Manganese	1.62

Analyses of Monel metal quoted by A. Stansfield,[2] C.E., in *Transactions of the Canadian Society of Civil Engineers* are as follows:

	Cast bar.	Rolled bar.
Nickel	68.90	67.55
Copper	26.55	26.25
Iron	3.30	3.25

On looking through the literature of the subject, no very recent analyses were found. The analyses of cast, rolled, and forged metal (given on page 355) were made at the laboratory of the Board of Water Supply, New York City, during the latter half of 1911.

For such a material as Monel metal, which is not a pure alloy, the feature of these analyses is the remarkable approach to uniformity in composition. If compared with the earlier published analyses, it would appear that the manufacturers have perfected the methods of reduction from ore and matte to such a degree as nearly to control the composition. In the present process of manufacture, the claim is made that the physical properties of Monel metal are not materially affected within the limits of variation in which the constituents occur. If this is true, a closer uniformity in the results of physical tests must be looked for from improvements in the heat treatment. As a matter of fact, the effect of variation in the copper-nickel ratio, as well as the influences of the presence of varying amounts of carbon, iron, silicon and manganese have not hitherto been studied, and are, therefore, not yet understood. A comparison of the chemical analyses with the physical tests made at the laboratory affords some deductions.

NICKEL-COPPER RATIO.

On looking over the results of the physical tests, it would seem that the variations found bear little relation to the chemical composition. Specimens of the cast metal in which the nickel-copper ratio was about the same, and other constituents in close agreement, gave a considerable difference in strength and yield point. For example, the specimen from heat 307 showed an ultimate strength of 69,100, and elastic limit 38,450, with a nickel-copper ratio of 68.49–27.02, while the specimen from heat 312 with a nickel-copper ratio of 68.10–27.04 and other constituents nearly identical, gave an ultimate strength of 73,750, and elastic limit 44,550. The difference of 10 per cent. in ultimate strength and 15 per cent. in elastic limit here is plainly due to some other cause than composition.

CARBON.

In accordance with previous examinations of this material, only the total carbon was determined in the samples submitted. With respect to the influence of this element, test 275, No. 1, gave ultimate strength 85,250, yield 51,250, and carbon 0.28. Same test, No. 2, showed ultimate strength 86,200, yield 58,250 and carbon 0.44, with other chemical constituents agreeing closely. Same test, No. 4, representing only a different section from the same rod, gave ultimate strength 85,500, yield 51,300, with carbon 0.37. The ultimate strength and yield in these three cases appear to follow in some measure the carbon content. In future study of Monel metal, it would be well to ascertain the carbon relations, for unless it is known in what form the carbon exists in the metal (whether free or combined, and in what ratio) it is fruitless to attempt deductions.

IRON.

Generally speaking, iron hardens, whitens and increases the strength of Monel metal, but reduces the elastic limit. In the tests on the cast metal, heat 301, with an iron content of 3.19 per cent., showed ultimate strength 71,600 and elastic limit 39,600. In heat 315, where the iron was 2.40 per cent., the ultimate strength was 66,800 and the elastic limit 46,950. In the rolled metal where the iron is high, the tensile strength is high, but with these tests, the limit of elasticity does not appear to follow any rule.

SILICON AND MANGANESE.

In the narrow limits of variation in which these metals were found, no indication was observed of any material effect on physical properties. Manganese is an advantage as a dioxidizer, and it serves a useful purpose in rendering harmless any sulphur that might be present, forming as it would manganese sulphide.

The results of the analyses in general show that the chemical composition alone is an insufficient guide to the strength or other physical properties of Monel metal, which depend, as in steel, so largely upon other influences, and especially heat treatment. Much light on these could be obtained from investigation with the microscope. A metallographic examination of the structure of the various specimens under test would be of great assistance in revealing segregation, the form in which the carbon is present, and other facts having an important bearing on the physical and chemical constitution of the metal.

While the laws governing the nickel-copper alloys are not thoroughly understood, some progress has been made in this study. There are no chemical compounds of copper and nickel, neither is there any eutectic mixture. The metals unite in all proportions without any separation on cooling. Hence, it is inferred that the two metals form solid solutions or mixed crystals in all proportions.

Working with pure metals, Hiorns[1] found that nickel dissolves in copper up to a certain percentage forming homogeneous solid solutions, and, on the other hand, taking nickel as the solvent, copper dissolves in nickel, forming homogeneous solid solutions up to a certain limit. These two solutions are

[1] *Metallurgical and Chem. Eng.*, **8**, 452.

[2] Canadian Society of Civil Engineers, *Transactions*, **23**, 302–309 (1909).

[1] A. H. Hiorns, on "Copper-Nickel Alloys," in *Metal Industry*, August and September, 1911.

miscible in all proportions. These facts have a direct bearing on observations made by David H. Browne,[1] Metallurgist of the Canadian Copper Company, after five years' study of copper matte and copper-nickel matte in the Bessemer converter, and in the manufacture of Monel metal. He submits the following conclusions:

1. Nickel-copper alloys act in the matte-blow like one metal.

2. Nickel-copper alloys follow during the matte-blow exactly the same laws that govern the behavior of copper alone.

Browne presents much data to prove that copper-nickel alloys form, as far as conversion is concerned, one homogeneous metal. In conversion, copper and nickel act together, presenting the same curious resistance to oxidation, and their relations toward iron are exactly similar to the relations of copper alone. The resistance to oxidation in the converter may be in some way connected with the resistance of the finished Monel metal to oxidation and corrosion. These facts seem to suggest the idea that the metal is an entity by itself.

As the component metals have never been separated from each other, the particles of each seem to be in more intimate contact than can be attained by any synthetic method of manufacture. It is claimed that melting the constituent metals together has produced no alloy having the same physical properties as the Monel metal obtained direct from the matte. The metal must therefore owe some of its remarkable properties to the grouping of its constituents. Small quantities of foreign substances which ordinarily affect the structure of alloys in general may be of negligible effect in an alloy of this type.

In certain of its chemical as well as physical properties, Monel metal closely resembles nickel. It is slowly dissolved by hydrochloric acid and by sulphuric acid, but dissolves rapidly in nitric acid with the evolution of nitric oxide. It is apparently unaffected by alkalies and shows the same stability as nickel in the presence of other corrosive chemicals. Like both nickel and iron, Monel metal is magnetic, a property which it loses above a certain temperature. Like nickel and iron, it absorbs carbon, and like steel, its physical properties are profoundly influenced, not only by the percentage of carbon, but the form in which it exists in the metal.

In the examination of Monel metal at the laboratory, the carbon present was observed in some samples in the free form as graphite, and in a smaller degree as combined carbon, the differential relations apparently depending as in iron on the rate of cooling.

PROPERTIES.

In appearance, Monel metal resembles nickel in color. It takes a brilliant polish, nearly equal to that of silver, which it retains indefinitely. On long exposure, the surface assumes a grayish cast, which may be removed with a polishing cloth. It is somewhat tougher than mild steel, but, nevertheless, it machines very easily. A lathe can be run at about the same speed on Monel metal as on mild steel, and the metal can be soldered, brazed, electrically welded, and successfully drawn.

[1] *Mining World*, **30**, 470.

SOME OF THE PHYSICAL CONSTANTS OF MONEL METAL.[1]

Melting point	1360° C. or 2480° F.
Specific gravity (cast)	8.87
Weight per cu. in. (cast)	0.319 lb.
Weight per cu. in. (rolled)	0.323 lb.
Coefficient of expansion, 20° to 100° C.	0.00001375 per 1° C.
Electrical resistivity temperature coefficient 0.0011 per 1° F. = 256 ohms per mil-foot.	
Electrical conductivity (copper 100 per cent.)	4 per cent.
Heat conductivity	1/6 of that of copper.
Shrinkage	1/4 inch per foot.
Hardness, cast material (Shore scleroscope)	20 to 23
Hardness, hot rolled rods (average Shore scleroscope)	27

A comparison of some of the properties of copper, nickel and Monel metal, as reported by a recent authority,[2] is given below:

	Copper rolled.	Nickel rolled.	Monel metal. Cast.	Monel metal. Rolled.	Monel metal. Annealed.
Tensile strength, lbs. per square inch	34,000	75,500	85,000	100,000	110,000
Elastic limit, lbs. per square inch	18,000	21,000	40,000	50,000	80,000
Elongation in 2 inches per cent.	52	43.9	25	30	25
Contraction, per cent.	57	57	25	50	50
Melting point	1084° C.	1500° C.	1360° C.		

Recent tests[3] of Monel metal at laboratory of William Sellers, Philadelphia, Pa., are:

	Hot rolled rods.	Sand castings.
Elastic limit, lbs. per sq. in.	58,873	37,427
Breaking strength, lbs. per sq. in.	86,899	78,236
Elongation in 2 inches, per cent.	40.0	38.5
Reduction of area, per cent.	60.5	34.0
Modulus of elasticity	22,000,000 to 23,000,000	

In all the technical reports relating to Monel metal, it is referred to as a non-corrosive alloy. Redfield[4] and other writers claim that the castings have the strength and many other properties of cast steel, while they have greater resistance to corrosion from sea water, superheated steam and corrosive chemical solutions than the bronzes. Owing to its remarkable stability in sea water, the government is now equipping its battleships with propellers of this material, these being cast in single pieces. Propellers have already been made for the North Dakota and for battleships of other countries, some of the latter being 15 ft. 6 in. in diameter in a single piece, weighing 16,000 lbs. After 18 months' service, it is said that the wear and corrosion of these propellers was found to be practically negligible. It was further found that they resist bending to such an extent that they are not so subject to loss of efficiency as propellers which yield under heavy backward pressure against the water.

Experiments made at the laboratory indicate that Monel metal possesses about the same resistance to corrosive action as the better known bronzes. Speci-

[1] Physical data in part from John F. Thompson, in *Eng. and Mining Journal*, **91**, 1911.

[2] *Transactions of the American Institute of Mining Engineers*, **41**, 310 (1910).

[3] *Ibid*, **1911**.

[4] S. B. Redfield, *American Machinist*, **34**, I, 513–514.

mens of several bronzes, Monel metal, and steel were weighed and embedded in rich earth, which was kept wet for six months by periodical additions of very dilute solutions of corrosive salts. At the end of the test period all the specimens were taken out, scrubbed, dried and weighed to ascertain the comparative loss from corrosion. The results were as follows:

	Per cent. loss.
Phosphor bronze	0.09
Tobin bronze	0.11
Monel metal	0.12
Parsons manganese bronze	0.12
Muntz metal	0.33
Steel	1.04

Another test of the same kind, under somewhat different conditions, but the same period, gave about the same relative results.

One advantage in favor of Monel metal in these tests was that it presented the least change in appearance as a result of the corrosive action.

CASTING.

While no trouble has been experienced in rolling Monel metal, considerable difficulty has been met with in some foundries in getting sound castings. Incidentally, it may be remarked that nickel-copper alloys have a great tendency to develop blow-holes on casting, due to occluded gases. This is another indication of the absence of a chemical compound, since the presence of a compound in an alloy seems to have the influence of preventing blow-holes, and closing the grain. Monel metal requires special precautions in casting on account of dissolved oxides and gases, which, if not removed, would render the ingots unsound. Successful castings have been made in small foundries by adding 2 ounces of magnesium per 100 lbs. of the alloy, before pouring.

Unsound castings may also arise from gases that are liberated in the cores of the patterns, and from the fact that the freezing point of the metal is so many hundred degrees above that of brass or bronze that these gases cannot escape before they are trapped by the freezing metal. This necessitates the use of the same methods as for fine steel castings. It must be remembered that the actual temperature of Monel metal cannot be much lower than 1550° C. The art of casting Monel metal is closely related to the art of casting steel, as distinct from the art of casting brass, bronze or cast iron. It really involves the art of handling the finest steel castings. The practice of casting Monel metal is, therefore, very similar to that followed in steel foundries. The melting equipment of the plant consists of standard reverberatory furnaces which are fired with oil, the fuel being fed by gravity. The metal is charged into the furnace in the form of pigs or slabs which are about 15 × 8 × 3 inches in dimensions, and weigh about 85 lbs. The melting point is about 2500° F. and eight hours are required to the heat. No fluxes nor alloys are necessary. Because of the relatively scant knowledge of nickel and its peculiarities, the handling of Monel metal requires expert attention in the melting.

The industry of making Monel metal castings is now past the experimental stage, and is being successfully accomplished in at least three foundries in New York and New Jersey. Mr. Leonard Waldo, consulting engineer, is authority for the statement that notable success has been achieved at the Johnson Foundry of Spuyten Duyvil in the casting of this metal. The Bayonne Casting Company, of Bayonne, N. J., and the Riverside Steel Company, of Newark, N. J., are other foundries that are making good castings.

USES.

Although a comparatively new alloy, because of its resistance to corrosion, its strength and the readiness with which it may be machined, Monel metal has already found many important uses. These include pump cylinders for handling salt water, propeller wheels, rudders, centre boards, deck fittings, mining screens, water ends of pumps, linings, valves, shafts, piston rods and plumbing fixtures subject to corrosive influences.

In the rolled metal, there is a wide range of usage. Striking instances in the past include the roofs of the new terminals of the Pennsylvania Railroad in New York, and the Chicago & Northwestern Railroad in Chicago, which were covered with Monel metal. The sheets have also been used on several large office buildings in New York, and on industrial plants subject to severe corrosive conditions where copper had proved unsatisfactory.

Rigid physical specifications should be the rule wherever Monel metal is considered for use in any form of engineering construction. With reference to chemical specifications, it would be impracticable to set any narrow limits as to chemical constituents, owing to the somewhat variable character of the ore and the method of manufacture. It is not believed, moreover, that such limits are necessary in order to insure the desired physical properties of strength and durability. If too close limits are set on chemical constituents, the metal so specified might be obtained, but at a cost that would render its use prohibitory.

LABORATORY, BOARD OF WATER SUPPLY,
NEW YORK CITY.

FREE LIME IN PORTLAND CEMENT.[1]

By H. E. KIEFER.

Received January 2, 1912.

It is to be regretted that the majority of chemists engaged in the manufacture of Portland cement have very little time for research work. Some of us have considerable time for experimental work, but the time and money spent are expected to produce commercial results rather than contribute to the stock of purely scientific knowledge. This latter we are compelled to leave to the research chemist, and as he usually lacks a practical manufacturing experience we may be able to supply a few facts and suggestions.

One of the most troublesome arguments which the cement chemist has to meet is on the subject of *Free Lime*. We hear it discussed by chemists and engi-

[1] Read at the Forty-fifth annual meeting of the A. C. S., at Washington, December, 1911.

neers and attribute all kinds of defects in the cement to it, yet it is very questionable whether any of us have a well grounded theory for the position we assume. We manufacture a product to meet certain specifications and when it fails in any of these we look for the cause and a remedy from a practical rather than a theoretical point of view, using theory only to facilitate results. A few things we know and many more we believe, hence we shall state first the general knowledge and follow it up with the theory and then add a few observations which may furnish suggestions for research chemists.

Constancy of volume is one of the requirements of practically all specifications. The test is made by subjecting a hardened pat to five hours' boiling in water in a loosely covered vessel or to the steam above the water in such a vessel. If the pat comes out sound and hard, with no signs of warping, checking or disintegration, the cement is considered sound. On the other hand, if it becomes soft, or warps or cracks on the edges it is considered unsound. From this point the theory begins. The explanation is that a failure to pass the test is due to free lime. Various quantitative methods have been suggested with a view of determining it, but so far as the writer knows none has ever given satisfaction. Microscopic tests have been suggested, but these likewise fail to be of any practical value. Some observations made in our laboratory lead to the belief that if free lime is a real cause it is not the only one, as there is a physical side which must be taken into consideration.

Le Chatelier says that if one per cent. of freshly calcined lime be added to a sound cement it will render it unsound. With this as a starting point, five well known American brands of Portland cement, which passed the boiling test as received, were taken and the above percentage of lime, freshly calcined over a blast lamp, immediately pulverized and added to the cement. None of them failed on the test. Larger quantities were than added, and with one brand 25% of freshly calcined free lime was required before the cement failed on the boiling test. The authority mentioned fails to say how finely the lime should be ground before adding to the cement, but it was presumed it should be at least as fine as the cement, hence it was quickly put through a 100-mesh sieve. The lime was obtained from a pure limestone at the highest temperature of a blast lamp. It might have been better to have used calcium nitrate as a starting point, but while these results are interesting, later tests showing the amount of water absorbed in passing from an unsound to a sound state shed a different light on the subject. The results of the tests are given in tabulated form.

In Table I are also given the analyses and the fineness of the cements to which reference will be made later. In one column are the results with lime sieved through a 100-mesh sieve and the cement as received, and in another column the cement after passing through a 200- and lime through a 100-mesh. It is necessary to explain that where "Boiled O. K." is used, it means the cement passed the test satisfactorily. To show degrees of soundness we use "Boiled 95 per cent." to mean checked slightly; "Boiled 90 per cent." to mean checked and softened slightly; "Boiled 85 per cent." to mean softened considerably; and "Boiled 80 per cent." to mean disintegrated entirely. These are only relative terms but they serve to indicate different degrees of soundness.

It will be noted in every case that the fineness of the cement played an important part, as when the particles coarser than 200-mesh were removed, the

TABLE I

No.	Brand	Age	Fineness. Percentages. 100-mesh.	200-mesh.	Cement as received and CaO through 100-mesh percentages. (a) CaO.	(b) H_2O.	Boiled.	Cement through 200 mesh and CaO through 100-mesh percentages. CaO. (a)	H_2O.[1] (b)	Boiled.
1	A	1 mo.	95.2	82.4	5.0	27.0	O.K.			
					6.0	28.0	90			
1		2 mo.			10.0	30.0	O.K.	12.0	34	O.K.
					12.5	33.0	95	15.0	35	95
					15.0	35.0	80	20.0	39	80
1		4 mo.			12.5	33.0	O.K.	15.0	35	O.K.
					15.0	35.0	95	20.0	39	90
					17.5	36.0	90			
					20.0	38.0	80			
2	A	1 mo.	97.5	85.5	25.0	45.0	O.K.			
					(c)					
3	B	1 yr.	96.0	79.0	5.0	27.0	O.K.	8.0	30	90
					6.0	27.5	95	10.0	33	80
					7.0	28.0	90			
4	C	1 yr.	93.0	75.4	6.0	27.0	O.K.	8.0	30	90
					7.0	27.0	90	10.0	33	80
5	D	1 yr.	96.8	78.6	6.0	27.0	O.K.	8.0	31	90
					7.0	27.0	95	10.0	36	80
6	E	1 yr.			12.0	29.0	O.K.	12.0	29	O.K.
					15.0	30.0	95	15.0	31	95
								17.5	33	80

(a) Per cent. of lime added.

(b) H_2O refers to the water used in making the pats.

(c) Greater amounts of lime made the pats too soft to be boiled after 24 hours.

ANALYSES OF CEMENTS.

No.	1.	2.	3.	4.	5.	6.
Loss on ignition[1]	3.08	2.80	4.60	5.19	3.20	6.27
SiO_2	21.28	20.80	19.24	20.26	22.00	19.68
R_2O_5	9.02	9.50	10.52	9.32	9.00	11.00
CaO	62.24	62.40	60.98	60.09	62.30	58.60
MgO	2.68	2.75	2.78	3.34	2.64	3.18
SO_3	1.61	1.56	1.55	1.54	1.23	1.54

cement stood larger additions of lime. The inference is that the fineness of the cement, the fineness of the lime and its degree of fusion play an important part. Unfortunately, brands B, C, D and E were all over one year old when tested, but it will be noted that brand A, one month old, 85½ per cent. passing a 200-mesh sieve, permitted 10 per cent. greater addition of freshly calcined lime than the same brand two months old, 82.4 per cent. fine and 2½ per cent. more than the same per cent. fine four months old, and that four coarser cements over a year old permitted the addition of less lime than the finer cement at two and four months.

Following this line and believing that the fineness of cement plays another part, a sample of cement

[1] The high loss on ignition in several of these brands is due to the long seasoning in bags.

80 per cent passing a 200 mesh sieve, which failed badly on the boiling test, was ground in a mortar to 85 per cent. fine and it showed improvement. In another portion ground 90 per cent. fine, the improvement was more marked and in a portion ground 95 per cent. fine the boiling test was perfect. We repeated this on various samples of cement with similar results. Thinking that possibly the free lime became hydrated from the moisture in the air while being ground, similar experiments were made by regrinding in a laboratory tube mill with a rubber gasket, so that the negligible amount of moisture in less than ½ cu. ft. of air would have a negligible effect on hydrating the free lime in 15 lbs. of cement used in the test. Results were similar. Sieving to various degrees of fineness in a small room where it was presumed the atmosphere was fairly dry, owing to the presence of a number of trays of cement and lime on which experiments were being made, gave similar results.

Table II gives the results of the average of five different samples of cement in each case, each treated in the following manner: grinding in a mortar, grinding in a tube mill and sieving. It will be noticed that the sample which was merely sieved to increase the fineness required a higher fineness as indicated by the 200-mesh sieve than the reground samples. This, of course, was to be expected:

TABLE II.—EFFECT OF FINENESS ON THE BOILING TEST.

	By regrinding in mortar. Boiling test. Per cent.	By regrinding in tube mill. Boiling test. Per cent.	Fineness regulated by sieving. Boiling test. Per cent.
81 per cent. passing 200 mesh, as received	80	80	80
After bringing up to 85 per cent. fine	85	85	80
After bringing up to 90 per cent. fine	90	90	85
After bringing up to 95 per cent. fine	O.K.	O.K.	90
After bringing up to 100 per cent. fine	O.K.	O.K.	95

It might be argued that the free lime was largely in the particles removed by the sieve, but this is offset by the tube mill experiments which were of exactly the same cement except as to fineness, as nothing was added or removed, and if the failure when 80 per cent. fine was due to free lime, the same free lime was present when it was 95 per cent. fine, and if checking is due to free lime, this free lime in the 95 per cent. fine was in a fine enough physical condition to become hydrated immediately on adding water when making the pat, or at least to become hydrated before the set had taken place. In the coarser samples it is possible that the free lime (if it is such) was present in the fused, glassy, coarser particles in such a way as to prevent its hydrating before the set had taken place, and the expansion took place on boiling the pat after it had hardened. The inference here is plainly that the degree of fineness is an important factor. The foregoing experiments apparently lead to the conclusion that a fair proportion of free lime is not injurious to a Portland cement if its physical condition is such as to permit it to be hydrated before the set has taken place. Hydrated lime is added to Portland cement with beneficial effect in some cases and it matters not if the hydrated lime is added afterwards or free lime is in the cement when used, provided it is in a condition to be readily hydrated, assuming that all other conditions of balancing the chemical composition and manufacturing details are properly regulated.

It is often noted that a sample of cement which fails to pass the test one day may pass it very satisfactorily several days later, and it has frequently been noted where the change from very poor to very good took place in 24 hours. In some cases where the pats completely disintegrated on boiling, the cement became sound in three or four days, while with several brands samples have required thirty days or more to become thoroughly seasoned.

An effort was made to find what change took place in the ultimate chemical composition when a cement passed from an unsound condition to a sound one. If it is due to a hydration of the lime by atmospheric moisture, then the amount of moisture absorbed would be a gage to the amount of free lime which had been hydrated, assuming (without any sound theoretical reason) that all the moisture taken up would go to hydrating lime and none of it enter into the complex reactions which take place when larger amounts of water are used. A number of experiments were made by determining the loss on ignition on unsound cements and making the same test after the cement became sound. A more correct method would have been to absorb the water given off on ignition, as it is well known that cement absorbs carbon dioxide on seasoning and this also is given off on ignition, but a glance at the results will show the relatively small total difference that even if we assume it all to be water used in hydrating lime the amount of lime hydrated is comparatively small:

6 tests showed a difference of 0.45 per cent. in loss on ignition between the unsound and sound condition of the cement.

6 tests showed a difference of 0.75 per cent.

6 tests showed a difference of 0.90 per cent.

Realizing the inaccuracy of the method, another set of experiments was conducted as follows: The unsound cement was placed on cover glasses and carefully weighed. This was placed on a rack under a bell-jar. A tray of water was placed below it and the whole set on an iron plate over a Bunsen burner. The bottom was sealed by piling finely pulverized flint (100-mesh and finer) around the lip of the jar so that the air could not be renewed during the test. The temperature was raised to 150° F. and kept there from periods ranging from one to twenty-six hours. A very great number of these tests were made and it was found that at 26 hours' heating, three samples of different cements absorbed 1.27 per cent., 1.84 per cent. and 2.02 per cent. moisture. All of these, as expected, passed the boiling test perfectly.

Repeated trials were made to determine the minimum amount of absorption necessary to pass from an 85 per cent. failing cement to a perfect test:

3 tests showed 0.10 per cent. was sufficient.
5 tests showed 0.19 per cent. was sufficient.
3 tests showed 0.24 per cent. was sufficient.
3 tests showed 0.27 per cent. was sufficient.

Whether these are the minimum amounts is open to question, as a number of tests showed practically no absorption, yet it is apparent that moisture is essential to seasoning. Unsound samples kept in sealed jars a year still remained unsound, and samples heated to 150° F. in dry air remained unsound, yet the above shows that a trifling amount of moisture produced the desired result. Moisture is essential and heat accelerates the action, as to be expected. At lower temperatures it is necessary to absorb considerably more water to get results than at 150° F. Coarse cements required more water and the problem becomes more complicated where the degree of burning of the clinker, the fineness of the raw material, and other manufacturing factors are taken into account.

Referring to the above tests where the minimum water was absorbed, it becomes apparent that in those cases, assuming all the moisture absorbed went to hydrating free lime, the maximum amount of free lime exerting the injurious influence could not have been over 0.31 per cent. Compare this with various amounts of free lime added, shown in Table I. It may be possible that the destructive expansion in the case of three cements requiring only 0.1 per cent. water in seasoning was caused by the hydration of its equivalent of 0.31 per cent. CaO, but it seems more probable that a physical explanation must also be considered in connection with it, for reasons briefly stated as follows:

Lime calcined at highest heat of a blast lamp is not injurious to soundness when added in reasonable amounts to Portland cements. Lime calcined at the temperature attained in a rotary kiln does not become fused, hence when pulverized with the clinker should hydrate readily on the addition of water.

In burning of Portland cement clinker, small particles of free lime may be encased in the fused mass of silicates, aluminates, etc. If subsequent grinding reduces this glass to a finely enough divided state, this lime will hydrate on addition of water and have no injurious effects. If free lime is the cause of disintegration, it seems that the state of fusion of the surrounding glassy clinker is directly responsible for it.

It is claimed that over-limed cements are most apt to fail on this test. It may be possible that owing to their being more difficultly fusible and requiring a higher temperature in the kiln, that a more glassy mixture envelops the free lime. This furnishes room for microscopic study.

Under-burned cements may fail on this test. Free lime is given as the explanation of this.

If free limes is the real cause, then the fact that as little as $^1/_{10}$ of one per cent. of moisture will rectify many bad cases, leads to the belief that the phenomenon of seasoning is not so much one of hydrating free lime as it is a decrepitation process in which heat and moisture break up glassy particles, putting the lime in a physical condition to be hydrated, but not necessarily hydrating it. Acting on this idea, it was believed that cements become finer with age. A number of tests seemed to confirm this, but the breaking of the small per cent. of coarser particles into finer ones takes place so slowly that differences of only one and two per cent. were obtained in sieving, which may not be sufficient to offset the possible personal error in the sieving process. To get at the hydrating or decrepitation results, whichever it may be, only the residues left on a 200-mesh sieve were taken and sieved until no more would pass. These were exposed to air and moisture and again sieved each week. The following table shows the fineness of a sample of cement, part of which was exposed to air and part kept in a sealed jar for varying periods. Residues from the same cement were placed in an open-jar and starting with nothing that passed a 200-mesh sieve, samples were sieved at various times, showing the per cent. passing the 200-mesh after decrepitation had taken place.

TABLE III.—SHOWING FINENESS ON A 200-MESH SIEVE.

	Sample exposed to the air. Per cent.	Sample kept in a sealed jar. Per cent.	Sample of residues kept in an open jar. Per cent.
Starting point.....	84.6	84.6	0.0
After 14 days.....	85.0	85.0	5.0
After 33 days.....	85.8	85.0	5.6
After 49 days.....	86.0	85.4	6.0
After 91 days.....	86.0	85.4	7.6
After 107 days.....	86.2	85.6	7.6

As was to be expected, the sample kept in air increased in fineness more rapidly than the one in the sealed jar, and while sieving tests are subject to some variation and inaccuracies, these samples were tested on the same sieve by the same man and by the same method, hence the personal error is probably about the same in each case. The results of the samples exposed to air might be explained by the theory of hydration of free lime, but those on sample kept in a sealed jar must be explained by a physical theory of disintegration.

SUMMARY.

While the work on this subject is by no means complete, it represents the results of some hundreds of tests and at the present time points to the following as worthy of consideration:

1. Only a thin film on the coarser particle of cement enters into the reactions on the setting of the same.
2. These coarser particles become finer with age.
3. The disintegration of these particles improves the soundness.
4. That if free lime is the cause of destructive expansion, three-tenths of one per cent. or less is sufficient to manifest itself.
5. That cases were noted where practically no absorption of water took place, hence cannot be explained by the hydration of free lime.
6. Cement kept in a sealed jar becomes finer with age, thereby indicating a mechanical decrepitation,

which, as tests show, becomes more pronounced in the presence of moisture.

7. Carbon dioxide from the air, while it may aid in seasoning, is not essential, as shown by several series of tests.

8. That increasing the fineness of any particular sample of unsound cement improves its quality in this respect.

9. With the foregoing data, it appears that the theory of free lime as the sole cause of unsoundness is not well founded.

10. Expansion may be due principally to physical strains in the coarser particles.

11. Any theory of expansion on a purely physical basis seems inadequate, inasmuch as pats may frequently remain in boiling water several hours or more before destructive expansion becomes manifest. If it were merely the different rates of expansion, one would expect the rupture to take place shortly after the boiling begins.

12. With the data in hand at present, a possible theory presents itself as follows: Seasoning of an unsound cement consists of decrepitation of the coarser particles, caused by or accelerated by heat and moisture, and that the moisture need not be in sufficient quantities to hydrate the free lime, but merely to render the coarser particles sufficiently fine to permit hydration before the set has taken place.

13. Le Chatelier claimed tri-calcium silicate to be the essential constituent of Portland cement and free lime as the agent destructive to soundness. Unger obtained *vitrified* tri-calcium silicate which disintegrated (seasoned), yet hardened well, while a *fused* tri-calcium silcate was unsound. This would indicate that if free lime is present in Portland cement, it is in the glassy unground particles.

14. O. Schott denied the existence of tricalcium silicates, tri-calcium aluminates, and tri-calcium ferrites in Portland cement, yet fused mixtures of these compositions showed the characteristic destructive phenomena found in unsound cements and which he attributed to free lime.

15. Michaelis claimed burning at too high temperatures produced unsound cements. Microscopic examinations of clinkers show a different physical structure of that from a rotary kiln and that burned at lower temperatures. The contradictory results obtained by investigators, both of synthetical mixtures and actual clinker, seem to be due to different degrees of fusion.

16. Shepherd and Rankin have demonstrated the existence of calcium tri-silicate, but the real cause of expansion is yet not conclusively proven.

17. What is needed now, in addition to the excellent work of the authorities herein mentioned and others unmentioned, is an investigation which will link together our knowledge on purely theoretical constitution of Portland cement clinker and the chemical and physical constitution of a commercial Portland cement, and further show what changes take place in passing from an unsound to a sound state.

THE CHEMISTRY OF ANAESTHETICS, IV: CHLOROFORM.

By Charles Baskerville and W. A. Hamor

Received December 14, 1911.

(Continued from the April No.)

2. THE CHANGES WHICH ANAESTHETIC CHLOROFORM UNDERGOES WHEN A CURRENT OF OXYGEN IS CONDUCTED THROUGH IT.

Among the anaesthetic mixtures, the combination of chloroform vapor with oxygen was used shortly after the introduction of chloroform as an anaesthetic, and it has recently been reintroduced into practice by Neudörfer, Kreutzmann, and others. It is stated by anaesthetists that oxygen does not antagonize the action of chloroform on the heart or nerve centers, but that it protects the patient from the dangers which result when chloroform is administered while his blood is in a condition of undue venosity[1] and that it prevents any intercurrent asphyxial condition. Gwathmey has stated positively[2] that oxygen increases the value of all inhalation anaesthetics as regards life.

It has been maintained, however, that chloroform undergoes alteration in this procedure. Falk[3] attempted to demonstrate that the passage of oxygen through chloroform[4] produces chemical changes in the anaesthetic. He reported that after the passage of oxygen for 20 minutes, changes could be recognized in the residual chloroform, in some cases hydrochloric acid and in others an acid with reducing properties[5] having been recognized. The quantities produced were found to be greater the higher the temperature and degree of illumination. This work is partially contradicted by the clinical results obtained by anaesthetists, and by the observations of Willcox and Collingwood[6] on the administration of oxygen bubbled through absolute alcohol.[7]

In order to determine whether the passage of a current of oxygen through anaesthetic chloroform results in the decomposition of the anaesthetic, 4 ounces of chloroform containing 0.70 per cent. by volume of absolute alcohol and 0.035 per cent. by volume of water, but otherwise pure, were placed in the chloroform container of the Gwathmey anaesthetic apparatus (Fig. 1), and a slow stream of oxygen was conducted through the chloroform for ten and one-half hours, at the end of which time $^3/_4$ ounce of chloroform remained. The experiment was conducted under the usual conditions obtaining during administration by the Gwathmey method, by electric light and at an average temperature of 20° C. The residue, upon examination, gave the following results:

[1] Buxton, *Anaesthetics*, 4th ed., p. 299.

[2] *Medical Record*, October 8th, 1910, p. 616. "On Chloroform-Oxygen Narcosis," see also Ziegner, *Münch. Med. Wochenschr.*, **57**, 2585; and Guarini, *Sci. Am.*, **90**, 24.

[3] *Deut. Med. Woch.*, **1902**, 862.

[4] The purity of this was not described, but it was evidently of the grade specified by the German Pharmacopoeia.

[5] Acetic acid, resulting from the oxidation of the alcohol in the chloroform used (?).

[6] *Brit. Med. J.*, Nov. 5th, 1910.

[7] Willcox and Collingwood stated that the administration of oxygen bubbled through absolute alcohol is a marked cardiac stimulant. It is especially important to note that they found the administration pleasant and non-irritating to the patient—that it causes no ill-effects to the lungs or bodily system.

Aldehyde.	Acidity.	Hydrochloric acid.	Sulphuric acid test.
None.	Acetic acid present.	None. No free chlorine.	Pronounced reaction. Faint reaction for odorous decomposition products and chlorinated decomposition compounds.

Oxygen was then passed through 4 ounces of chloroform containing 0.56 per cent. by volume of absolute alcohol and 0.03 per cent. by volume of water, but otherwise pure, for three and one-half hours, after which time 2 ounces of chloroform remained. The intensity of illumination and temperature conditions were identical with those of the preceding experiment. The chloroform residue contained no free chlorine or hydrogen dioxide; no hydrochloric acid or carbonyl chloride; no acetaldehyde; but it showed the following changes:

Acetic acid: 0.00045 gram in 100 cc.

A marked response with sulphuric acid, intensified on the addition of formalin. Although a faint reaction for chlorinated decomposition products was obtained, the reaction with sulphuric acid was attributed to oxidation products of the alcohol present.

These experiments showed that when chloroform of the present pharmacopoeial strength and purity

FIG. 1.

is administered in conjunction with oxygen, no decomposition of the chloroform occurs, and that the oxidation of the alcohol present would not give rise to products which would affect the results of anaesthesis, provided the vapors are passed through water which absorbs the oxidation products. The results obtained also support the views previously expressed with regard to the oxidation of anaesthetic chloroform.

In order to ascertain whether the oxidation products of alcohol are removed by passage through water[1] and whether any oxidation products responding to the test with sulphuric acid are carried over by the vapor of the chloroform, the following experiment was performed:

Oxygen was passed through $3^1/_2$ ounces of chloroform containing 1 per cent. of 95 per cent. alcohol, but otherwise pure, for four and one-half hours, the oxygen-chloroform vapor being conducted through four ounces of water kept at 20° C. The resulting chloroform vapor was condensed, and after $1^3/_4$ ounces of chloroform had passed through the water, the experiment was discontinued. The examination of the residue and condensed chloroform showed the following:

Acidity (acetic acid	
Chloroform used	none.
Residue in container	0.00015 g in 100 cc
Condensed chloroform	none.
Sulphuric acid test	
Chloroform used	negative.
Residue in container	marked reaction.
Condensed chloroform	negative.

Therefore, it was concluded that the oxidation products of alcohol are not carried over when the chloroform-oxygen stream is conducted through water, and that these are concentrated in the residue. This applies, of course, only when the conditions usually followed in practice are observed.

3. THE DECOMPOSITION OF CHLOROFORM VAPOR UPON EXPOSURE TO GAS LIGHT, ETC., DURING ADMINISTRATION.

The occurrence of untoward symptoms during the administration of chloroform in rooms in which gas is burning,[1] or where there are other varieties of naked flames,[2] or strong electric light,[3] has been frequently reported; consequently, it has been urged that surgical operations be not performed by gaslight.[4] As to just what products are formed, there is a difference of opinion. Iterson[5] considered that there occurred a combination of the chloroform vapor with the combustion gases, whereas Hartmann[6] and Waddelow[7] observed an odor of chlorine, Von Langenbeck considered that "chlorocarbonic acid" was formed, and Breaudat found hydrochloric acid and an acrid oil. At all events, when a mixture of chloroform vapor and air is decomposed by a flame, irritating compounds are formed.[8]

4. THE EFFECT OF AGITATION UPON ANAESTHETIC CHLOROFORM.

Tunnicliffe[9] concludes that when chloroform is

[1] Such a procedure is followed when the Gwathmey apparatus is used in practice.

[1] One of the earliest references to the decomposition of chloroform by exposed flames is in the *China Med. Missionary J.*, Dec., **1888**, 160. Iterson, Fischer, and Zweifel drew attention to this decomposition in 1889, and in that year Patterson narrated personal experiences (*Practitioner*, **42**, 418). See also, *Lancet*, March 12th, **1898**, *Birmingham Med. Rev.*, August, **1892**; but especially, Schumburg, *Apoth.-Ztg.*, **13**, 758; Gerlinger, *Ibid.*, **17**, 314; and Eisenlohr and Fermi, *Ber.*, **1892**, 585. Soubeiran and Liebig had observed that a mixture of chloroform and alcohol, in equal measures, burns with a smoky flame and pungent odor.

According to Ramsay and Young (*Jahresber.*, **1886**, 628), the vapor of chloroform, when passed through a red-hot tube, yields hexachlorbenzene (C_6Cl_6), perchlorethane (C_2Cl_6), and some perchlorethylene (C_2Cl_4).

Löb (*Z. Elektrochem.*, **7**, 903) reported that when a wire was heated to redness by an electric current in the vapor of boiling chloroform, hydrochloric acid and tetrachlorethylene were the principal products of decomposition at comparatively low temperatures, hexachlorbenzene and hexachlorethane and chlorine appearing also at higher temperatures. The tetrachlorethylene is probably formed by polymerization of dichlor methylene, the primary product of the pyrogenetic decomposition.

[2] Oil lamps and candles (Waddelow, *Pharm. J.*, [4] **6**, 324).

[3] Buxton (*Anaesthetics*, **1907**, p. 180) states that he observed that chloroform decomposes when a powerful electric lamp is held over the inhaler. Cf. Schoorl and Van den Berg, *Pharm. Weekblad*, **43**, 47, who show that air is necessary for such decomposition.

[4] *E. g.*, by Von Langenbeck (see *Pharm. Ztg.*, April 6, **1889**, 221).

[5] *Ibid.*

[6] *Ibid.*

[7] *Loc. cit.* See also, Wardleworth, *Pharm. J.*, [4] **14**, 376.

[8] *Lancet*, **1899**, 1, 1728; *Therap. Gaz.*, **1899**, 601; Breaudat's *Diet. Physiologie*. Cf. Ragsky, *J. prakt. Chem.*, **46**, 170.

[9] *J. Roy. Army Med. Corps*, **2**, No. 4, 459.

initially pure, except for added alcohol, it remains free from "pharmacological deterioration" under the ordinary conditions of military transport, providing that the bottles are kept closely stoppered and protected from strong light.

The authors subjected unopened, brown glass bottles of the following anaesthetic chloroforms to intermittent agitation for 206 hours in a Spiegelberg shaking apparatus, in such a way that considerable mechanical shock was imparted to the chloroform:

1. A three-ounce bottle of chloroform manufactured from acetone, containing 0.5 per cent. by volume of absolute alcohol and 0.025 per cent. by volume of water, but otherwise pure and of full pharmacopoeial grade.

2. A two-ounce bottle of chloroform manufactured from acetone, containing 0.8 per cent. by volume of absolute alcohol and 0.05 per cent. by volume of water, but containing a trace of extractive matter from the cork stopper.

3. A two-ounce bottle of chloroform containing 0.97 per cent. by volume of absolute alcohol and about 0.05 per cent. of water, but otherwise pure.

4. A two-ounce bottle of chloroform manufactured from acetone, containing 0.7 per cent. by volume of absolute alcohol and about 0.04 per cent. of water, but otherwise pure.

All of these samples were well stoppered and were, in every respect, identical with chloroform as it is supplied to the trade. The samples numbered 2, 3, and 4 contained more air space than No. 1, this being especially marked in the case of Nos. 3 and 4.

When the samples were examined after agitation for 206 hours, the following results were obtained:

Sample.	Acidity.	Hydrochloric acid or chlorides; chlorine and hydrogen dioxide.	Sulphuric acid test.	Odorous decomposition products.	Chlorinated decomposition compounds.
1.	.....	None	Pronounced reaction	None	Very faint reaction
2.	.....	"	Pronounced reaction	"	None
3.	0.00045 g. acetic in 100 cc.	"	Decided reaction[1]	"	Faint reaction
4.	0.0004 g. acetic in 100 cc.	"	Marked reaction[2]	"	"

From these experiments, the following conclusions were drawn:

1. When anaesthetic chloroform is subjected to agitation accompanied by mechanical shock, the alcohol present undergoes oxidation, the extent of this being dependent upon the amount of air present, the nature of the agitation, especially its violence and length, and the light exposure. The above experiments were all made in daylight at 20° C.

2. Impurities decomposable by sulphuric acid are formed under such conditions, these resulting both from oxidation of the alcohol and, when unprotected cork stoppers are used, from the extraction of resinous matters from the stopper or luting. "Chlorinated decomposition compounds" may form, although we are inclined to attribute the response had for their presence to oxidation products of alcohol in this case.

Since these conclusions apply to anaesthetic chloroform of the present *United States Pharmacopoeia* degree of purity and strength, care should be exercised when such chloroform is shipped for considerable distances, or is kept at sea, that a minimum amount of air is present; in case glass-stoppered bottles are not used, that the cork stopper is capped to prevent extraction and shrinkage; and that the succussion to which chloroform is likely to be subjected, is neither of an intense nor protracted nature.[1]

5. THE PRESERVATION OF CHLOROFORM.

(a) *Preservation with Alcohol.*

As early as 1857 it was pointed out by Squibb[2] that an addition of alcohol to chloroform was the best means of preventing decomposition; it appears that the practice, one which he considered of importance, originated with him some years previously. Squibb observed that chloroform of the density above 1.497 had a marked tendency to decompose, and that the decomposition became inevitable above 1.498. Therefore, he suggested reduction in specific gravity to 1.49 or at least 1.494, by the addition of ethyl alcohol. Later[3] Squibb stated that his experience was that "pure" chloroform to which 0.625 per cent. of alcohol had been added might be kept for ten years in ground-stoppered bottles of amber glass without a trace of decomposition.

In 1863, David Brown, of the British firm of J. F. Macfarlan & Co., finding that samples of chloroform which rapidly decomposed were invariably of the density 1.50, while those which kept well were of slightly lower density, suspected that the small proportion of alcohol present in the last-mentioned was the cause of the preservation. Ever since this time, it has been the British custom to reduce chloroform to the density 1.497 or thereabout, which procedure, it has been maintained,[4] has given satisfaction and is a necessary one.

Shortly after the observations of Brown, Maisch,[5] after a series of experiments on the action of light on chloroform, arrived at the following conclusions: In order to preserve "pure" chloroform of the specific gravity 1.49, it should be kept totally excluded from the light; and to keep chloroform in the daylight, it should be reduced in specific gravity by the addition of about two fluidrachms of 95 per cent. alcohol to one avoirdupois pound of chloroform of the density

[1] The cork stopper of this container was capped with tin, hence no extraction could occur.

[2] As in [1].

[1] See Part 6 of this section, where the *Storage* of chloroform is discussed. Further reference to the subject of extraction will be made when the *Test with Sulphuric Acid* is referred to.

[2] Paper read before the New York Academy of Medicine in that year; see *Am. Med. Month.*, July, 1857.

[3] *Ephemeris*, **4**, 1431.

[4] See Dott, *Pharm. J.*, [3] **15**, 703. Also, Clark, *Ibid.*, [3] **12**, 740. Symes and Mason (*Ibid.*, **8**, 893) also testified that small quantities of alcohol considerably enhance the keeping qualities of chloroform. Brown (*Ibid.*, **25**, 865) was of the opinion that the specific gravity of chloroform should not be under 1.497 at 15° C. Such chloroform contains 0.25 per cent. of alcohol and, according to Brown, if kept out of the sunlight and otherwise properly stored, may be kept many years.

[5] *Proc. Am. Pharm. Assn.*, **1867**.

1.492. Maisch found that when chloroform had been reduced in specific gravity to 1.475 or less, the presence of several drops of water in the bottle would not induce the liberation of "chlorine" after an exposure of two weeks in direct sunlight. He considered that this amount of alcohol (about forty drops in one fluid ounce) would not be objectionable when the chloroform was used as an anaesthetic.

The preservation of chloroform with ethyl alcohol has also been insisted upon by German[1] and French[2] authorities. In fact, it may be said that the addition of alcohol, in amounts varying from 0.25–1.00 per cent., has been generally favored and that such an addition is universally practiced.[3]

The amounts of alcohol stated as permissible in the various official chloroforms intended for anaesthetic purposes are as follows:

Belgium	1.0 per cent.
Denmark	1.0 per cent.
France	0.005 part by weight.
Italy	0.5 per cent.
Sweden	0.5–1.0 per cent.
Switzerland	1.0 per cent. absolute.
United States	0.6–1.0 per cent.

The *British Pharmacopoeia* does not define the quantity of alcohol permitted, but specifies that the chloroform be worked to the density 1.490–1.495.[4] The amounts allowed in the anaesthetic chloroforms of countries other than those mentioned above, may be determined from the specified densities;[5] thus, in Holland and Russia, a mere trace of alcohol is permitted at the outside limit.[6]

However, it should be mentioned that, although the addition of small amounts of alcohol to chloroform has been pharmaceutically recognized as necessary, several have expressed a negative opinion.[7]

[1] Hager (*Year-Book of Pharm.*, **1870,** 119) recommended the addition of 0.75–1.0 per cent. of alcohol, and stated that it served as a preservative for any definite period. According to Schact and Biltz (*Pharm. J.*, **1893,** 1005), an addition of alcohol amounting to one part in four hundred of chloroform (0.25 per cent.) is sufficient to prevent recognizable decomposition for one month or longer; with double that amount (0.5 per cent.), decomposition is prevented for nearly a year; and with 1 per cent. for many years. We may say, however, that these are only average statements, liable to variation in both directions, according to the effects produced by the varying intensity of light, and only being applicable to chloroform properly stored and contained in bottles having a minimum amount of air present.

[2] Regnauld (*J. Pharm. Chim.*, [5] **10**) found that alcohols have a preservative action on chloroform, toluol being most effective. Behal and François [*J. Pharm. Chim.*, **5,** 417 (1897)] considered that the addition of a small amount of alcohol as a preservative should be permitted.

[3] In this connection, see *British Pharmacopoeia*, **1885,** 109; Jolles, *Chem. Ztg.*, **11,** 786.

[4] In 1878, British manufacturers reduced the chloroform of density 1.497–1.500 by the addition of about 1 per cent. of absolute alcohol. The *British Pharmacopoeia* of this time allowed chloroform of the density 1.49, thereby admitting the addition or presence of such an amount of alcohol as some claimed would be prejudicial to administration. The *United States Pharmacopoeia* allowed chloroform of the density 1.480, and, as a result, the American chloroform was regarded by some as adulterated and quantities were imported at this time.

[5] See Table II under *Specific Gravity*.

[6] As a matter of fact, however, the anaesthetic chloroform used in these countries contains at least 0.25 per cent. of absolute alcohol, according to our determinations of the density and quantitative estimations of the alcohol present.

[7] Du Bois-Reymond (*Sci. Am. Suppl.*, No. 839, p. 13413) considered that alcohol was of no use when impurities were present and was unnecessary when the chloroform was pure. Helbing and Passmore (*Helbing's Pharm. Record*, March, 1892) concluded from the few experiments which they made on the decomposing influence of sunlight, that the value of the addition of absolute alcohol to pure chloroform was questionable. All of these investigators *assumed* that the chloroform which they termed "pure" contained no alcohol.

Mialhe[1] even regarded the presence of absolute alcohol in chloroform as deleterious.

The authors have demonstrated in Part I of this section that ethyl alcohol retards the decomposition of pure chloroform and that pure chloroform readily decomposes into oxidation products of a deleterious nature—in fact, it becomes toxic—unless so preserved. Those who hold a contrary opinion have evidently failed to conduct experiments under conditions conducive to oxidation and have misunderstood the function of alcohol, as well as other preservatives, in the oxidation process. The value of having *pure* anaesthetic chloroform for use and the importance of its proper storage cannot be gainsaid—in fact, these conditions are conceded as necessary ones by those who have had occasion to inquire into the changes which chloroform undergoes when carelessly stored or kept for long periods; but we are convinced that the presence of pure alcohol in pure chloroform is both a precaution and a necessity, and that small amounts of alcohol in no way interfere with the physiological action of chloroform.

(*b*) *Preservative Agents Other than Alcohol.*

Inorganic Preservatives.—Boettger[2] found that chloroform which had undergone decomposition by exposure to sunlight might be purified by agitation with sodium hydroxide, and stated that when chloroform was placed in contact with sodium hydroxide it might be preserved indefinitely. Newman and Ramsay[3] recommended a similar treatment, namely, the use of lime, both for purification of decomposed chloroform and as a preservative. Brown,[4] however, found that the method of Newman and Ramsay was unsatisfactory.

Allain[5] stated that although the addition of alcohol or ether to chloroform somewhat retarded the formation of carbonyl chloride and hydrochloric acid, it did not altogether prevent it. He learned that sulphur, purified by digesting for 24 hours with ammonia and then carefully washed and dried, would effectually prevent the decomposition of chloroform.[6] Temoin[7] reported that chloroform, to which 0.4 per cent. of sulphur had been added, underwent no alteration on keeping, even when exposed to light.

Dott,[8] considering that oxygen was essential to the decomposition of chloroform by light and that chlorine was always present at the earlier stages of the alteration,

[1] *Pharm. J.*, **7,** 345. Mialhe found that chloroform acquired caustic properties when mixed with a small quantity of absolute alcohol, and concluded that chloroform used in medical practice which caused vesication of the lips and nostrils contained a certain quantity of anhydrous alcohol, the presence of which was suspected by Soubeiran and Gerdy. Mialhe thought that the alcohol might act by combining with and coagulating the albuminous fluids of the body.

[2] *Bull. de Therap.*, May 15, 1864.

[3] *Lancet*, Jan. 23, 1897.

[4] *Pharm. J.*, **61,** 669; *Mon. sci.*, **53,** 423.

[5] *Chem. Ztg.*, **19,** 310.

[6] In a sample saturated with sulphur, after exposure to sunlight for four months, no impurities could be detected and the sample produced a "normal anaesthesia."

[7] *Pharm. Centralh.*, **45,** 872; *Chem. and Drug.*, **64,** 973.

[8] *Pharm. J.*, [4] **2,** 249.

regarded it as probable that sulphur acted as a reducing agent, and that any substance slightly soluble in chloroform and readily oxidizable would likewise act as a preservative. Experiments with morphine, gallotannic acid, and hypophosphorous acid confirmed this view.

Organic Preservatives.—Masson[1] found that poppy-seed oil exerted a marked preservative action on chloroform. A specimen containing 0.1 per cent. was exposed to direct sunlight for 21 days, at the end of which time there was no decomposition; and one with 0.2 per cent. of the oil, kept in ordinary light, showed no decomposition in three years. From Masson's own observations on the preservative powers of alcohol,[2] one would conclude that he considered it perfectly satisfactory.

Breteau[3] devised a method for the prevention of the alteration of chloroform in the air and light, and of indicating finally the decomposition, which consisted in adding to the chloroform from 5–10 thousandths parts of one of the following bodies: pith of elder, cork or coniferae; and 3–5 thousandths parts of guaiacol, ionone, spermaceti, cholesterol, terpineol, citronellic acid, geranic acid, etc. He stated that the elder pith might be impregnated with a solution of a material colorless in chloroform, and dry, this material, as congo red, undergoing a change of tint under the influence of the decomposition products of chloroform. Congo red was stated to be very desirable, since it turns blue, and gradually decomposes, when the alteration is decided. Later Breteau mentioned the following substances as preservatives of chloroform in addition to those just mentioned: ethyl alcohol and ethyl ether, nitrobenzene, methyl and amyl salicylates, thymol and coniferin. As "indicators," he stated that cellulin and gelatin might be used in addition to dyestuffs, and that the "indicator" might also consist of a dyestuff which changes color in the presence of the decomposition products of chloroform.[4] Still later he stated that the "indicator" might be interposed between the chloroform and the stopper of the container, or might be fixed to the stopper, or might even form the stopper. Cinnamic acid and inositemono-methyl ether were added to the list of preservative agents.[5]

Breteau and Woog[6] have published the results obtained by using the preservatives and "indicators" devised by Breteau. They found that by the use of 2–4 parts per 1000 of oil of turpentine,[7] purified spermaceti, menthol, terpineol, citronellol, geraniol, amyl and methyl salicylates, guaiacol, thymol, safrol, ionone, or methyl-protocatechuic aldehyde, chloroform could be preserved in white glass bottles in diffused light. It was also learned that a number of "indicators" showed the acidity of chloroform undergoing incipient decomposition before it was sufficiently developed to affect silver nitrate.[1]

There can be no question of the value of some, if not all, of the preservatives proposed by Breteau, but, so far as the authors are able to learn, his method of preservation has not been adopted by manufacturers of anaesthetic chloroform, mainly owing to the fact no doubt that the value of ethyl alcohol is established.

Preservation in an Inert Gas.—Mouneyrat[2] devised a method for the prevention of the decomposition of chloroform, involving storage in special apparatus in an atmosphere of nitrogen.[3] This method might serve for the storage of samples of pure chloroform.

(*c*) *Role of Alcohol in the Preservation of Chloroform.*

Schacht and Biltz[4] found that not only did an addition of ethyl alcohol arrest decomposition that had already commenced, but that it would, with sufficient agitation, remove the "free chlorine" that had been eliminated, as well as the carbonyl chloride formed. They found that the amount of alcohol requisite for that purpose depended upon the extent to which decomposition had advanced, and hence they concluded that the length of time during which alcohol would protect chloroform would always be proportionate to the amount of alcohol added. According to this view, so soon as the amount of alcohol is consumed, by the joint action of the "free chlorine" and the carbonyl chloride directly resulting from the decomposition of chloroform, the products of the change that has gone on up to that point without injurious consequences become all at once recognizable, just as if the alteration had suddenly commenced. At that point, Schacht and Biltz found that the presence of "free chlorine" and carbonyl chloride, the "initial products of the decomposition," could be detected. To account for the presence of hydrochloric acid, Schacht and Biltz state that since hydrochloric acid will also have been formed by the subsequent reaction of the "free chlorine" with alcohol, that acid will also become recognizable as soon as the last trace of alcohol disappears, although it will at first be dissolved by the alcohol present. In the opinion of Schacht and Biltz, these successive changes afford an explanation of the fact that chloroform containing alcohol will, in the first instance, evolve hydrochloric acid,

[1] *J. Pharm. Chim.*, [6] **9**, 568.

[2] Masson considered that the preservative action of alcohol on chloroform was demonstrated by the condition by the samples at the *Pharmacie Centrale* in 1899, where specimens containing only 0.1 per cent. and exposed in yellow glass bottles in a window to diffused light, were found to have kept "perfectly" after standing for ten years.

[3] French Patent 353,858, 1905.

[4] First Addition to French Patent 353,858, 1905, dated June 20, 1905.

[5] Second Addition to French Patent 353,858, 1905, dated Nov. 18, 1905.

[6] *Compt. rend.*, **143**, 1193.

[7] The use of oil of turpentine as a preservative of the chlorides of carbon has been patented by Pichon and Truchelut (French Patent 402,235 of 1909).

[1] Breteau and Woog stated that an elder pith disc dyed lightly with congo red and left in the bottle of chloroform would serve to indicate decomposition by a change in color to blue. Since congo red is very sensitive and is insoluble in chloroform, such a procedure may be followed and the method may prove to be advantageous in hospitals, etc.

[2] French Patent 370,991, 1906.

[3] Mouneyrat found that decomposition was prevented by storing chloroform in closed bottles, *e. g.*, siphons, under a pressure of pure nitrogen gas, and he described a special container which might be filled and emptied for use in an inverted position. The neck of the bottle is fitted with a screw valve; when it is required to fill the bottle, the air is exhausted by a vacuum pump and pure nitrogen is admitted. This process is repeated several times, until every trace of oxygen has been expelled. The bottle, still in the inverted position, is then placed in connection with a supply of chloroform, which is drawn through the valve, owing to the vacuum which exists in the bottle. When partly full, the valve is closed, the bottle is brought to an upright position, and pure nitrogen is forced in at a pressure of 3–4 atmospheres.

[4] *Pharm. J.*, **1893**, 1005.

originating indirectly from the reaction of "chlorine" with alcohol, and soon afterwards "free chlorine" and carbonyl chloride, originating directly from the decomposition of chloroform.[1]

Brown,[2] commenting on the views of Schacht and Biltz, in which these chemists attributed the preservative action of alcohol on chloroform to the formation of harmless products by the action of the primary decomposition products on alcohol, quoted experiments to show that "free chlorine" and carbonyl chloride might be readily detected in chloroform before the added alcohol had been consumed; and further that such chloroform yielded only a very faint reaction with silver nitrate, at the time when a very marked one was obtained with zinc iodide and starch. He concluded, therefore, that the preservative action of alcohol must be ascribed to some other cause; and that it was folly to attempt to arrest decomposition in chloroform altogether by the excessive addition of alcohol.

Since Adrian[3] also considered that the products of the decomposition of pure chloroform are carbonyl chloride, water, and chlorine, and then carbon dioxide and hydrochloric acid, it was natural that he should hold a similar view of the function of alcohol in preservation. Adrian found that the presence of alcohol did not, strictly speaking, prevent the decomposition of pure chloroform; but that it retarded it, and "fixes the nascent chlorine," forming, instead of free hydrochloric acid and toxic carbonyl chloride, other chlorine derivatives which are harmless to the animal organism. According to him, the first phase of this reaction is that of "free chlorine" on alcohol, as represented by

$$C_2H_5OH + Cl_2 = CH_3.CHO + 2HCl.$$

The acetaldehyde thus formed has a great affinity for chlorine, giving acetals more or less chlorinated until finally, by successive stages, trichloraldehyde, $CCl_3.CHO$, is formed. The hydrochloric acid liberated during these reactions, according to Adrian, combines also with the alcohol, forming esters, providing the alcohol is in excess; if not, it is found as free acid. Adrian found that in two years pure chloroform would liberate 0.034 per cent. of free chlorine, and from 0.011-0.015 per cent. in six months; therefore, he concluded that the addition of one part of alcohol in one-thousand of chloroform was sufficient to ensure preservation. He also considered that sulphur and almond oil doubtless acted in a similar manner by "fixing" the "nascent chlorine" as it was liberated.

Thus it will be seen that Schacht and Biltz and also Adrian believed that chloroform itself decomposed in the presence of alcohol, although Adrian admitted that the decomposition was retarded by alcohol. Schacht and Biltz thought that alcohol acted by forming harmless products with "chlorine" and carbonyl chloride, while Adrian was of the opinion that alcohol combined with the "free chlorine," forming finally trichloraldehyde. Schacht and Biltz did not, so far as their investigations indicate, examine exposed anaesthetic chloroform to learn whether oxidation products of alcohol were present; and Adrian, although he apparently found acetaldehyde, misinterpreted the nature of the oxidation process, considering that chloroform decomposed in the presence of alcohol. Since we have shown that free chlorine is not a primary product of the oxidation of pure chloroform, and that no alteration of the chloroform itself occurs while sufficient alcohol is present to be itself oxidized, the explanations offered by these investigators are not satisfactory. We do not deny that free chlorine and carbonyl chloride may be eliminated from decomposed pure chloroform by the addition of, and agitation with, alcohol—in fact, we have found that carbonyl chloride may be thus partially, at least, removed—and it is also likely that chlorinated derivatives of the oxidation products of alcohol may form after the chloroform itself commences to oxidize; but we have shown that the chloroform itself is not subject to decomposition while alcohol is present, and that the primary products of the oxidation of anaesthetic chloroform are the oxidation products of the alcohol present. The objection of Brown to the view of Schacht and Biltz may be explained by the fact that oxidation products of alcohol give certain alcohol reactions; for example, the iodoform test of Lieben and the chromic acid test, considered as indicative of the presence of alcohol by Brown, show the presence of acetaldehyde in chloroform. The explanations advanced by Schacht and Biltz and also by Adrian, to account for the presence of hydrochloric acid in anaesthetic chloroform after the alcohol present had been consumed, may be accounted for by the fact that they considered that chlorine, and not hydrochloric acid, is a primary product of the oxidation of pure chloroform; this is not in accord with our experience.

The authors are firmly convinced that the experimental evidence supplied in Part 1 of this section offers a correct explanation of the decomposition of pure chloroform and of the changes which occur when anaesthetic chloroform is oxidized, and that this is fully substantiated and discussed in Parts 2 and 4. These results showed that the explanations of the function of alcohol and of other preservatives in retarding the decomposition of chloroform were incorrect, and therefore the authors were obliged to take a totally different view of the role of alcohol in this oxidation process.

(d) *The Authors' Theory of the Mechanism of Preservation.*

Stadlmayr[1] considers that alcohol acts as a "catalytic retarding agent," thereby delaying the decomposition of chloroform. Undoubtedly it modifies the reaction velocity of the oxidation, of which deportment we have analogous cases.

[1] On the other hand, Schacht and Biltz considered that the decomposition of pure chloroform commenced by giving rise to carbonyl chloride, water, and chlorine, and then carbon dioxide and hydrochloric acid, at once. This view was also held by Brown

[2] *Pharm. J.*, **1893**, 321.

[3] *J. Pharm. Chim.*, **18**, 5. Cf. the similar view of Benrath (*Ann.*, **382**, 222), who maintains that alcohol does not "protect" chloroform from decomposition, but simply renders carbonyl chloride harmless.

[1] *Z. angew. Chem.*, **23**, 1847

The retardation of the oxidation of phosphorus by the vapor of organic compounds is well-known,[1] as is also the retardation of the formation of ammonium carbonate by alcohol vapor;[2] but there is a remarkably similar case of retardation of oxidation by means of organic compounds, namely, in the oxidation of sodium sulphite.

Bigelow[3] has found that if a solution of sodium sulphite is oxidized by drawing through it a current of atmospheric air, the velocity of the oxidation is greatly reduced by the presence of small quantities of alcohol, etc. Here also the influence of the retarding agent is found to be additive. From Bigelow's investigation it may be concluded that the influence of the retarding "catalyst" is not on the dissolution velocity of oxygen, but on the reaction velocity. The only reason, however, that Bigelow gave for terming the retardation of the speed of oxidation a "catalytic action" was that considerable retardation was caused by small amounts of substance. In no case did he present evidence to demonstrate that the retarding substance remains unchanged or that a small amount of it will suffice to effect the retardation of the reaction for any considerable period of time. All the substances which he found retarded the oxidation of sodium sulphite (primary and secondary alcohols, polyatomic alcohols, phenol, aniline, ether, acetaldehyde, benzaldehyde, benzene, turpentine, etc.) were, if we consider the organic retarding agents alone, non-oxidizing agents; and the substances which did not retard were not reducing agents or but very poor ones. Therefore, it appears that the retardation of the oxidation, in this case at least, is ascribable to the reducing power of the substances added. Such a view is strengthened in part by the investigations of Young,[4] who found that the presence of relatively small quantities of "poisonous substances," especially alkaloids, reduced the rate of the oxidation of solutions of stannous chloride by means of free oxygen; and who later[5] presented evidence tending to lead to the conclusion that oxidations by means of free oxygen are subject to inhibition by small quantities of foreign substances, that probably all organic substances possess inhibitive action, and that this effect is not instantaneous but develops somewhat slowly with the oxidation of the solution. In these investigations, as in that of Bigelow, it was not determined whether or not the inhibiting agent remained unchanged, but the principal fact brought out—namely, that the inhibitive effect develops with the oxidation of the solution—shows that here we have a case of so-called "negative catalysis" and that the inhibitory action is a chemical one. This view is supported by the work of Titoff,[6] who learned that mannite acts as a "negative catalyst" in the oxidation of aqueous solutions of sodium sulphite, and that the retardation is proportional to the amount of mannite present.[1]

From the preceding we may draw the following conclusions:

It is well established that certain organic compounds exert a retarding influence on the reaction velocity of oxidation processes. The retardation at least in the cases considered—is due to the reducing power of the organic compounds, and consequently the inhibitive action is a chemical one. The retardation is proportional to the amount of inhibitor present.

Since it has been shown that the oxidation of chloroform is retarded by the presence of alcohol, for example, and that the period of retardation is dependent upon the amount of alcohol present;[2] and particularly since we have demonstrated that the decomposition of chloroform itself is prevented so long as oxidation of any alcohol present proceeds, we offer the following explanation of the preservation of chloroform.

The preservative action of alcohol is due to the combination of the "retarder" with certain of the reacting substances; and any substance soluble in chloroform and readily oxidizable will exert an inhibitory effect on the oxidation of chloroform itself. All compounds which have been found to serve as preservatives of chloroform are reducing agents, and the effect is only due to their capacity for oxidation. In the case of alcohol, inhibition develops with oxidation and retardation results until the oxidation of the inhibitor reaches a maximum. Thus, when chloroform is "preserved" with alcohol, the preservative is gradually consumed and is eventually totally destroyed, after which the decomposition of the chloroform itself proceeds as in the case of pure chloroform, with the exception that chlorinated derivatives of the oxidation products of alcohol may result.

6. THE STORAGE OF ANAESTHETIC CHLOROFORM.

Chloroform required for anaesthetic purposes should always be furnished in vials, bottles or dropper-ampoules of anactinic glass containing about the quantity sufficient for one narcosis, and at the most not more than can be used within several days. A two-ounce bottle is of sufficient size, and the use of a fresh bottle of this capacity which has been properly stored is an assurance that the anaesthetic has not become contaminated. Nevertheless, the user should always assure himself of the good faith of the manufacturer. If, however, for any particular reason chloroform is ordered in a large container, *e. g.*, in hospitals, it is advisable, immediately after opening it, to subdivide the entire remaining contents into two-ounce bottles, taking care to fill the small bottles completely. It is important to see that the bottles are completely free from water, and empty bottles should not be refilled without thoroughly cleansing and drying them. In no case should chloroform be gradually withdrawn in small quantities from large bottles or

[1] Berthellot, *J. de l'Ecole Polyt.*, **3**, 274; Graham, *Quart. J. Sci.*, **6**, 83; Davy, *Edinb. Phil. J.*, **15**, 48; Centnerszwer, *Z. physik. Chem.*, **26**, 1.

[2] Van't Hoff, *Studien*, 1896, p. 36.

[3] *Z. physik. Chem.*, **26**, 493.

[4] *J. Am. Chem. Soc.*, **23**, 140.

[5] *Ibid.*, **24**, 326.

[6] *Z. physik. Chem.*, **45**, 641.

[1] Cupric sulphate causes the oxidation to proceed with a measurable velocity, thereby accelerating the main reaction; but when mannite is present, the positive catalyst is destroyed by chemical union with the retarder.

[2] Reference is had only to the components of *pure* anaesthetic chloroform.

carboys. When it is found necessary to store anaesthetic chloroform, it should always be kept in a cool, dark place, in well-filled, or, better still, completely filled, tightly stoppered bottles of anactinic glass.[1]

Containers.—It has been shown[2] that colorless glass protects chloroform less than red or yellow glass, and in practice brown glass bottles are now exclusively used.[3] Chloroform should not be kept in black bottles, because it is difficult to learn when these are perfectly clean and dry. If colorless bottles are used for any reason, these should be provided with an opaque covering and kept in a dark place. All glass containers should be made of high-grade glass,[4] which should show no alkaline reaction when the bottle is filled with distilled water containing several drops of phenolphthalein solution and heated at 100° C. for six hours.

A question of importance in the trade is, "What marked advantage have glass bottles over soldered tins?" The question of keeping anaesthetic chloroform in tin containers has been a much agitated one in the Federal War Department, and within the last ten years this Department has decided in favor of the tin container.

The opinion of the authors is that glass containers are to be preferred, since any foreign matters present may be readily observed and the bottles then cleaned. In the case of tins, greater care must be exercised to ensure a non-contaminated chloroform, especially since some of the flux used in soldering may be accidentally introduced and thus impart an acid reaction to the chloroform. As mentioned previously, hydrochloric acid accelerates the decompositon of chloroform.

Since it has been stated that spirit containing 95–96 per cent. by volume of ethyl alcohol is perfectly indifferent to tin, and tin and tinned metals are absolutely unattacked by 90 per cent. denatured spirit, the tinned metals only being corroded where the tin layer is broken,[5] one would conclude that acid-free chloroform,[6] containing the usual amounts of alcohol and water, would also be without action on tin, providing it is stored in tin containers, having no broken or scratched surface, very carefully capped, and with a minimum amount of air. In order to determine this, a five-pound sample of chloroform containing 0.84 per cent. by volume of absolute alcohol and approximately 0.05 per cent. of water, which had been stored in a tin container, sealed, for sixteen months, was examined for the presence of tin. This sample left a residue non-volatile at 100° C. amounting to 0.0220 gram per liter, but none remained upon ignition and no tin could be detected in the sample. The examination of a sample of anaesthetic chloroform which had been kept in a sealed tin for six years also showed that no tin had been dissolved. In both cases, however, *oxidation of the alcohol present had occurred*, although no decomposition products of chloroform were present.

We have been informed by a prominent manufacturer of chloroform that he has "demonstrated that moist chloroform in the presence of a metal will slowly form traces of CH_2Cl_2, and . . . . probably . . . . that it is possible to distil pure, dry chloroform in a metal container and produce a decomposition, as shown by the following formula: $4CHCl_3 + Cu_2 = C_2Cl_6 + 2CH_2Cl_2 + Cu_2Cl_2$. This reaction, however, takes place so slowly that it would never be noticed except in the handling of a material on which superlative efforts have been expended for years in order to get the last extreme of purity." Moreover, "all chloroform contains traces of CH_2Cl_2." In view of this, therefore, it would seem that there is another reason for preference in the matter of container. In this connection, it should also be mentioned that it is probable that all metals which show anomalous anodic conductivity are likely to develop free hydrogen dioxide in contact with water and oxygen.[1]

Stoppers for Glass Containers.—The *Pharmacopoeia of the United States* formerly required the use of "glass-stoppered" bottles, but subsequently changed this to "well-stoppered" bottles, thus allowing the use of cork-stoppers, a practice which has become general in this country,[2] owing to the consequent reduction in cost.

The objections which have been urged against the employment of cork stoppers are two in number: first, the chloroform penetrates the cork after some time, especially during the agitation incidental to shipment, causing shrinkage and consequent leakage; and second, organic matter is extracted from the cork.[3] To obviate these difficulties, certain manufacturers have adopted the plan of covering the bottom of the corks with tin foil,[4] a procedure which has been found to be satisfactory, while others use a paper or parchment covering.[5]

[1] "On the Storage of Anaesthetic Chloroform," see also *Bull. Pharm.*, **20,** 215; *National Dispensatory*, **1887,** p. 439; and Merck's *Annual Report*, **16,** 42.

[2] See Part I of this section, cf. Madsen, *Pharm. J.*, [4] **18,** 747.

[3] All of the manufacturers of chloroform in this country use brown glass ("anactinic") bottles. Of the eight different makes of German chloroform examined by the authors, only two were contained in colorless bottles.

[4] "On the Action of Alkalies on Chloroform," see Berthelot, *Bull. soc. chim.*, [2] **29,** 4; André, *Compt. rend.*, **102,** 553; de St. Martin, *Ibid.*, **106,** 492; Mossler, *Monatsh.*, **29,** 573. It appears to be well established that potassium hydroxide in alcoholic solution will slowly decompose chloroform.

[5] Heinzelmann, *Z. Spiritusind.*, **27,** 399. Malmejac, however, [*J. Pharm. Chim.*, **13,** 169 (1901)] found that a small amount of tin goes into solution in 95° alcohol after six months.

[6] "On the Action of Hydrochloric Acid in Chloroform on Tin," see Patten, *J. Phys. Chem.*, **7,** 161, who found that the dry solutions acted upon the metal less violently than upon zinc or aluminum, but more violently than on lead.

[1] Barnes and Shearer, *J. Phys. Chem.*, **12,** 155, 468. However, hydrogen dioxide is not formed on shaking finely divided zinc, magnesium or aluminum with water when all traces of free oxygen are excluded (Kernbaum, *Compt. rend.*, **152,** 1668).

[2] In Germany, however, glass-stoppered bottles are used by prominent producers of anaesthetic chloroform (Kahlbaum; de Haen; Merck; A.-G. für Anilin-Fabrikation).

[3] Consequently it was found difficult to meet the sulphuric acid test prescribed by the Pharmacopoeia. Cf., however, *Am. J. Pharm.*, **1868,** 289.

[4] At present such a protection is used by three American firms. Since adopting this plan, these firms state that no complaints regarding leakage or conformity to the sulphuric acid test have been received. When metal coverings are used on the stoppers of chloroform containers, they should be made rather of thin sheet metal, than of foil, since we have found that tin-foil becomes broken or displaced, and often separates from the stopper when it is withdrawn from the bottle. Failure to do this has been the cause of some complaint. If the plan mentioned is followed, the use of glass-stoppered bottles will not be found necessary, even though the trade should become willing to pay the advanced price for such packages.

[5] Such a plan has been adopted by one American firm and three German producers.

Allain[1] and Masson[2] have recommended that when chloroform is kept in cork-stoppered bottles, a lute of "bichromate gelatin" should be used to prevent leakage. This is totally unnecessary when a proper stopper is used, and the employment of lutings on the stoppers has led to many differences between the manufacturer and consumer in the past.[3] Only one of the many samples of anaesthetic chloroform examined by the authors was contained in a bottle having a luted cork stopper, and in this case, although the chloroform itself was pure, considerable of the resinous matter had been extracted, and, as a result, the chloroform failed to comply with the sulphuric acid test, which, as will be shown later, is one of great importance.

VII. The Impurities of Anaesthetic Chloroform.

1. CHEMICAL CONSIDERATIONS.

In conducting an examination of anaesthetic chloroform with the view of ascertaining its suitability for the production of anaesthesia, one must test:[4]

A. For impurities which the chloroform brings with it from the manufacturer. These are usually the so-called "organic impurities," which are found in considerable amounts in a chloroform which has been made from poorly rectified spirit, acetone, or carbon tetrachloride (the sources), if impure chemicals have been employed in the manufacture or subsequent rectification and purification, or if the chloroform has not been properly purified. These impurities, even though some may not be of much importance from a physiological standpoint, must still be given attention, since an impure chloroform is more likely to become altered through oxidation during storage, notwithstanding the fact that pure ethyl alcohol has been added. So far as we have been able to learn, the adulteration of anaesthetic chloroform is not practiced now,[5] and crude chloroform is not often sold as chloroform of anaesthetic grade.[6]

To summarize, the possible impurities of this class are as follows:

Excess water;
Excess alcohol;
Acetone;
Methyl alcohol;
Carbon tetrachloride;
Tetrachlorethylene, hexachlorethane, etc.;
Aldehydes, chloral;
Amyl, propyl, and butyl alcohols and compounds;
Ether;[1]
Acids (sulphuric, hydrochloric, formic, acetic);
Metallic chlorides;
Ethyl chloride;
Ethylene chloride;
Ethylidene chloride;[2]
Ethyl acetate;
Oils ("empyreumatic," "pyrogenous," "chlorinated");[3]
Fixed and extractive matter.[3]

B. For the oxidation products of chloroform and alcohol; in other words, it must be ascertained if the chloroform has been properly stored. The possible impurities of this class are as follows:

Acetaldehyde;
Acetic acid, formic acid;[4]
Carbonyl chloride;
Hydrochloric acid;
Hydrogen dioxide;
Chlorine;
Chlorinated derivatives of alcohol oxidation products.

The detection and, where necessary, the estimation of the impurities embodied in these two classes, will be discussed in succeeding sections of this paper.

2. PHYSIOLOGICAL CONSIDERATIONS.

Huchard[5] has said: "Pure chloroform, well given to a patient prepared for it, almost never kills." Serious results have occurred from the use of anaesthetic chloroform containing foreign substances, and although the grades at present sold as chloroform for anaesthesia hardly contain impurities which can be held responsible *per se* for deaths which have occurred during narcosis, yet the presence of these may produce some, at least, of the disagreeable after-effects so often noticeable following the administration of some chloroform. Consequently, anaesthetic chloroform should comply with the most rigid tests,[6] and the preparation which conforms with these requirements and at the same time is comparatively less likely to decomposition than others also answering the same tests, should at all times be preferred to a cheaper but less stable grade. According to the investiga-

[1] *J. Pharm. Chim.*, [3] **9,** 571.

[2] *Ibid.*, [6] **9,** 568. According to Masson, the "bichromate gelatin" is thus composed: Solution A—gelatin, 100; distilled water, 300; glycerin, 10. Solution B—potassium dichromate, 20; distilled water, 200. Two parts by weight of the first are mixed with one part by weight of the second, both previously being warmed; the mixture should be kept at 55–60° on a water bath during use.

[3] Some of these will be referred to when the *Test with Sulphuric Acid* is discussed.

[4] This summarization is given in order that the reader will observe the propriety of all consumers of chloroform of assuring themselves, by examination, that the chloroform they purchase and use or dispense is pure, notwithstanding the fact that, as a rule, chloroform of inferior grade, frequently encountered about 1880 (see Perrin, *Pharm. J.*, [3] **9,** 614; and Champion niere, *Ibid.*, [3] **12,** 623), especially in France, is now rarely represented as being of anaesthetic grade. This is largely due to the stringency of many of the pharmacopoeias, but is in part to be ascribed to the experience and integrity of the manufacturers. It sometimes happens, however, that chloroform is declared to be impure, by surgeons following a fatality from its use in particular, when this is not the case. For an example, see the experiences of Blum, *Pharm. J.*, [4] **19,** 103. "On the Organic Impurities of Chloroform," see Stadlmayr, *Pharm. Post*, **43,** 418.

[5] Cf., however, Baird (*Proc. Mass. Pharm. Assn.*, **1906,** 59), who examined six samples of chloroform in 1904, and found one "adulterated."

[6] But this appears to have been practiced as late as 1885 in this country, since Davenport (*Am. J. Pharm.*, [4] **16,** 111) reported that fourteen out of fifteen samples of chloroform examined by him in that year were the crude article.

[1] From 1865–1875, ether was considered as one of the general contaminants of chloroform.

[2] About 1880, ethylidene chloride was regarded as a general impurity of chloroform.

[3] See *Tests for Odor and Residue.*

[4] According to Benrath (*Ann.*, **382,** 222), chloroform in aqueous suspension or aqueous alcoholic solution is oxidized to formic acid or its decomposition products when exposed to ultra-violet light.

[5] *J. des Praticiens*, May 31, 1902.

[6] The pharmacopoeial tests are, in general, insufficient, and samples of chloroform may comply with the tests prescribed by various pharmacopoeias and yet important differences may be shown to exist among them by means of other tests. These facts have been brought out by Langgaard (*Therap. Monatsh.*, May, 1902), and the opinions and results obtained by the authors will be given in subsequent sections of this paper.

tions of Feigl and Meier,[1] the customary chemical examination of a sample of anaesthetic chloroform is not conclusive, but requires confirmation by biological tests. Most important, however, is clinical experience.

In regard to the fatal results which have been obtained in practice following the use of chloroform vapor for the induction of anaesthesia, a considerable percentage of cases, especially those where death has ensued immediately upon first inspiration, may not be due to the action of chloroform at all.[2] However, Simpson[3] enumerates a number of cases antedating the general introduction of anaesthesia which may be classed as "chloroform deaths.[4]"

In all indubitable cases the nature of the chloroform administered certainly plays an essential role; this fact is supported by convincing evidence, even though the percentage of deaths caused by chloroform administered during operations is unaccountably different in different years, times, and places.[5] We can attribute the existing diversity of opinion on the subject only to the degrees of purity of the anaesthetic used, the different modes of administration, the varying lengths of the time of the anaesthesia, the varying severity of the operation, and the state of the patient.

According to almost all authorities, the first danger from the use of chloroform consists in an interruption of respiration;[6] and it has been said that only after the observation of the pulse had superseded that of respiration did chloroform deaths become more frequent.[7] Experience has therefore clearly shown that every obstacle to respiration must be removed; the presence of irritating contaminants in the anaesthetic must, as a consequence, be guarded against.[8] In France, Sedillot,[9] who laid the greatest stress on the purest chloroform, did not have to record a single death; but in nine-tenths of all the chloroform deaths on record, not a word is said in regard to the degree of purity of the anaesthetic employed, and consequently an important factor for forming an opinion is entirely excluded.[10] Hence the published statistics are not to be relied upon.

Dubois-Reymond[1] appeared to have experimentally demonstrated that impure chloroform is dangerous. Therefore, to the rules for administering chloroform so often given, he considered that one omitted by all but Sedillot and his school should be added, namely: That the quality of the chloroform be carefully examined, and only the very best procurable be employed for anaesthesia.

There can be no question but that Dubois-Reymond obtained results which indicated rather a difference of degree than of kind between the action of pure and impure anaesthetic chloroform. He insisted that the impurities acted as cardiac depressants;[2] but, as was noted at the time,[3] it does not appear that by their removal *pure* anaesthetic chloroform[4] ceases to hamper circulation.[5] That the impurities are ordi-

[1] *Biochem. Z.*, **1906,** 316. Feigl and Meier marked out the blood-pressure curves on a drum by means of a kymograph, healthy dogs were made to inhale equal quantities of chloroform of different makes through a tracheal canula. The results obtained showed that the different brands of chloroform, although they appeared almost identical by the chemical tests, differed considerably in their liability to cause a diminution in blood pressure and to cause arrthythmia of the pulse-beat.

[2] See in this connection, Nussbaum, *Handb. d. Allg. u. Spec. Chir.*, **1867,** 612; Lawrie, *Lancet*, **1890,** i, 149.

Brit. Med. J., **1870,** i, 199.

[3] Sansom (*Chloroform*, London, 1865) put the average mortality at 0.75 per 10,000; Richardson (*Med. Times and Gaz.*, **1870**), at 2.8, and Morgan (*Med. Soc. Va.*, **1872**), at 3.4.

[4] One of us (C. B.) in conjunction with Dr. J. T. Gwathmey is securing complete data from every hospital in the United States.

[5] Metcalfe (*Trans. N. Y. Acad. Med.*, **1**, 145) stated in 1850 that his experience, extending then to 800 administrations, went to substantiate the fact that the use of impure chloroform causes headache, nausea, and bronchial irritation.

[6] Hewitt, *Proc. Roy. Med. and Chir. Soc.*, 890.

[7] Occhini (*Pharm. J.*, [3] **8,** 988) came to the conclusion that the tolerance of chloroform could be assured by the preventive use of ammoniacal inhalations. Although chloroform and ammonia have a mutually antagonistic action of the heart, according to Ringer (*Practitioner*, **1881,** 19), such a method is unnecessary if *pure* chloroform of anaesthetic grade is properly administered to a patient prepared for it.

[8] *Bull. soc. Chir.*, **7,** 1881.

[9] Some exceptions may be noted here. Dr. Hunter McGuire, surgeon in the Confederate Army during the Civil War, one time remarked that chloroform had been administered 40,000 times in his corps alone without a single death, and he attributed the result largely to the splendid grade of chloroform which the Union Army had supplied him (almost all the chloroform used by the Confederate Army was captured from the Federals, although some of English manufacture came through a blockade). The results of an examination of a sample of chloroform of this period will be given later in this paper.

In 1882, Preston (*Pharm. J.*, [3] **12,** 982) recorded that there had occurred 53 deaths in 152,260 administrations, and that in these 53 cases the impure chloroform had something to do with the fatal results. Atthill (*Brit. Med. J.*, **1892,** i, 110) stated that he had administered chloroform in over 2000 cases and considered that it is essential for its safe use that the chloroform be pure; he mentioned that the chloroform in general use at that time was often impure.

Chisolm (*Sci. Am. Suppl.*, No. 642, 10259), who had in 1888 a record of 10,000 cases of general anaesthesia with chloroform and no deaths, recorded his experiences, but made no mention whatsoever of the purity of the chloroform used.

[1] *Brit. Med. J.*, **1892,** i, 209.

[2] The report of the Hyderabad Commission shows that deaths from chloroform are more frequently due to its checking the power of respiration than to the arrest of the heart's action; see, in this connection, *Lancet*, **1890,** i, 149, 421, 486, 1140, 1369; **1890,** ii, 356; *Brit. Med. J.*, **1891,** ii, 1080, 1121. Indeed, Lawrie states (*Chloroform*, **1901,** 15) that the doctrine that chloroform has no direct action on the heart must be considered as finally established. This is supported by the results of the biochemical observations of Feigl and Meier (*Biochem. Z.*, **1906,** 316), who concluded that narcotic doses of pure chloroform have little or no action on blood pressure, the heart, or the circulatory system in general; and that these effects, when observed, are usually due to the accompanying impurities in commercial alcohol. Some observations, however, seem to indicate that chloroform has an action on the circulatory system, although in these cases the purity of the anaesthetic was not always considered. Cf., for example, Filehne and Biberfeld, *Z. f. exper. Path. u. Therap.*, **3,** 171 (1906); these investigators discuss the advisability of adding volatile analeptics to chloroform to prevent the reduction of blood pressure. Also, Busquet and Pachon (*Compt. rend. soc. biol.*, **66,** 90) reported fibrillation of guinea-pig's heart under the influence of chloroform. Schaefer and Scharlieb (*Proc. Physiol. Soc.*, **1903,** 17) have insisted on the specific nature of the action of chloroform on cardiac muscles. Embley and Martin (*J. Physiol.*, **32,** 147) have found that the action of chloroform in the blood in such quantities as may occur with inhalation of 1–3 per cent. of vapor in air, paralyzes the neuro-muscular mechanism of the blood vessels. Tissot (*Compt. rend.*, **142,** 234) reported that more than 70 mg. of chloroform per 100 cc. of arterial blood often causes death. It appears that chloroform forms a loose combination with haemoglobin; for a discussion of the physical chemistry of anaesthesia, wherein this is discussed, see Moore and Roaf, *Thompson, Yates and Johnston Lab. Rept., Liverpool*, **1905–6,** 151–94.

Waller (*Nature*, **76,** 403) "tested purified chloroform against the concentrated residue of its impurities, and found the former to be more powerful than the latter;" he did not, however, lay any stress upon the fact that anaesthetic chloroform can be of variable quality. Tunnicliffe (*Pharm. J.*, [4] **18,** 515) subjected samples of anaesthetic chloroform to mechanical shaking for several days, then exposed them for a considerable time to direct July sunlight, and finally allowed them to evaporate in the laboratory to one-half bulk; the residual portion did not differ at all from pure chloroform in its toxic action on cardiac muscle (!).

[3] *Brit. Med. J.*, **1892,** i, 236.

[4] "Chloroform Pictet" was taken as the example.

[5] See above and also Charteris and MacLennan, *Brit. Med. J.*, **1892,** i, 679, who believed that differently manufactured chloroform, although conforming to the tests specified by the *British Pharmacopoeia*, might have different actions, and that possibly some of the dangers were due to the employment of impure chloroform.

narily very slight, Dubois-Reymond admitted, but he contended that, although really infinitesimal in quantity, they act strongly in chloroform solution.

From his experimental investigations and deductions, we learn that there are undoubted impurities which are able to intensify and hasten the lethal properties of chloroform, but we cannot definitely assert just what these are. We know, however, what the general likely impurities of anaesthetic chloroform are; and if proper precautions are taken to guard against their presence, untoward symptoms should not follow the proper administration of anaesthetic chloroform. In succeeding sections of this paper, tests to which such chloroform should comply will be given.

(*To be continued in the June No.*)

TESTING METHODS OF RUBBER CONTENTS IN RAW AND VULCANIZED RUBBER.

By W. A. Ducca.

Received January 5, 1912.

Two distinct chemical compounds of the rubber molecule have been the subject of extensive investigation during the last ten years, regarding a possible usefulness for a direct determination of caoutchouc in a given sample of raw or of manufactured rubber—the nitrosites or nitrosates as nitrogen compounds, and a compound with bromine as tetrabromide.

Harries deserves the credit of being the first one to make an attempt in the direction of a distinctly defined nitrogen compound. Almost simultaneously with C. O. Weber, he began a study of the action of nitrous acid gases upon solutions of rubber in benzole. Weber, who unfortunately did not live to finish his experiments, worked with nitrogen dioxide, developed by heating nitrate of lead. He obtained, or at least claimed to have obtained, an addition product of two molecules of NO_2 to one molecule of rubber of the formula $C_{10}H_{16}N_2O_4$ in a polymeric form. The compound would have to be classed as a nitrosate. Harries on the other hand applied N_2O_3, generated from nitric acid and arsenic trioxide. He stated that by varying the conditions he was able to separate three distinct compounds of a nitrosite character which he called nitrosites (*a*), (*b*), and (*c*).

It is not the purpose of this paper to enter into a detailed discussion of these well known classical investigations, but the true composition of the compounds obtained in the reactions is of the utmost importance for the estimation of pure caoutchouc in a given sample of rubber. I, therefore, feel justified in giving a short review of the more important results reached by different authors and at different times.

Harries' three nitrosites are as follows:

Nitrosite *a*, $C_{10}H_{16}N_2O_3$, is formed by a six-hour action of dry N_2O_3 upon a 1 per cent. solution of rubber.

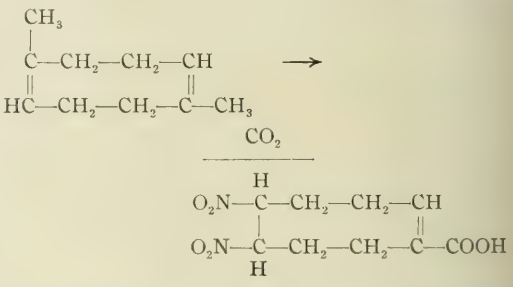
Nitrosite *b*, $C_{10}H_{15}N_3O_8$, is formed when dry N_2O_3 gas is passed from two to three days through a suspension of nitrosite *a* in benzole.

Nitrosite *c*, $C_{10}H_{15}N_3O_7$, is precipitated from a 1 per cent. rubber solution in benzole by the action of wet N_2O_3 gases.

His first statements were later modified in some respects by Harries himself. The ultimate product of the action of N_2O_3 gas upon 1 per cent. solutions of rubber in benzole was claimed to be uniformly nitrosite *c*, provided the reaction were allowed to go on for a sufficiently long time. Contrary to his first report, he gave as the best way to prepare this compound the use of N_2O_3 gas thoroughly dried over phosphorus pentoxide.

These results naturally induced Harries to apply the new compound for an analytical determination of caoutchouc. He obtained a satisfactory result on a sample of an uncured rubber compound, but did not make any attempts to develop the method any further, as this would hardly be within the scope of his work as a college professor, and should rather be accomplished by a technical man. His work in this direction was taken up where he had left it by a number of investigators; they practically all reached different conclusions based on various results.

The most exhaustive study of the subject was undertaken by Alexander with rather surprising results, not in accordance with Harries' observations. The action of N_2O_3 was shown to go much further than had been observed by either Weber or Harries. His method of precipitating the nitrosites from the rubber solution differed from Harries' method in so far as he generated nitrous acid anhydride from starch and 80 per cent. nitric acid. The formula of the final product was given as $C_9H_{12}N_2O_6$, containing one carbon atom less than the original rubber molecule. This fact was explained by the oxidation of one of the two methyl groups of the caoutchouc molecule to carbonic acid gas, while the other one is supposedly oxidized only to the carboxyl group COOH.



That this explanation is possible from a theoretical standpoint is open to discussion. In support of his theory Alexander mentioned his observation of carbonic acid gas during the reaction. He certainly made a very thorough study of the matter, both theoretically and practically, and his analytical results are hardly to be doubted. On the other hand Gottlob, who undertook a careful re-examination of Harries' experiments, comes to the conclusion that their results were correct beyond any doubt and that he could confirm them in all respects. In his opinion, Alexander obtained different results only by not closely following Harries' method in every detail. We conclude from these contradicting statements, that it is, to say the least, very difficult to obtain

uniform results, a fact which is not surprising at all. Weber very justly pointed to the indefinite composition of nitrous acid gases. It seems perfectly natural that under such conditions indefinite reaction products will result. Furthermore, every chemist working with these nitrosites or nitrosates will experience the practical impossibility of determining their purity by the ordinary well known tests. Ultimate analysis by combustion, therefore, does not yield reliable information as to their true composition; the figures obtained are likely to represent the mean percentages of carbon, hydrogen and nitrogen in several distinct compounds. In accordance with my own experiences, I fully support Alexander's latest views: The nitrosate method is not of real value, at least not at the present time, for the estimation of actual caoutchouc in either raw or vulcanized rubber. For the determination of the vulcanization coefficient it may prove to be an excellent method. Here it is not obligatory to know the exact composition and purity of the nitrosate, which is used only as a means to completely precipitate the sulfur of vulcanization. Of course, this question cannot be considered as definitely settled and it will require a long and careful study of all the conditions before it can be established as a well founded fact to hold true in any case and for any form of soft vulcanized goods.

The advantage of the method for the latter purpose consists chiefly in the elimination of the many troublesome fusions with the soda-potassium carbonate and potassium-nitrate mixture, especially unsatisfactory in presence of a large percentage of mineral matter. The precipitate can be finely powdered and is therefore applicable for rapid sulfur determination by ignition with sodium-peroxide, whereby the sulfur is oxidized to sulfuric acid in the form of sodium sulfate which in turn can be precipitated as barium sulfate. The sample has naturally to be first extracted with acetone in the usual way to remove free sulfur; any vulcanized oils are separated by saponification. One-half gram of the sample, thus prepared, is treated with 50 cc. of kerosene (boiling point up to 300° C.) until completely dissolved. Mineral matter can be removed either before nitrosation by centrifuging the kerosene solution or afterwards by pouring it with the nitrosate on a filter, and dissolving the rubber compound in acetone whereby the mineral matter is left on the filter. The acetone solution is either evaporated to dryness, or poured into cold water to separate the nitrosate in a crystallized form. The latter method will secure a purer material but necessitates an additional filtration. It is very essential to pour the acetone solution into water and not the water into the acetone, and to have the water cold, else the nitrosates will separate in an oily layer which does not crystallize very well and is, therefore, hard to filter. The resulting yellow powder is mixed with sodium-peroxide in suitable proportions and ignited in the usual way, as for instance in coal analysis for the determination of sulfur.

The tetrabromide method for the direct determination of caoutchouc was originated by Budde, and naturally received much more general attention on account of its less complicated nature and greater rapidity. Originally designed as a gravimetric method, it has undergone several changes, necessitated by the results of a number of investigators. But, even at the present time, it has not been developed to such a degree of accuracy as to deserve universal recognition. One fact stands out clearly: All possible sources of error have been laid bare, so that the investigator when trying to apply the method for his special purposes can easily recognize all difficulties and obstacles he is liable to encounter. The investigations published in connection with this problem, finally leading up to the present status of the tetrabromide method, form a very interesting chapter in the history of the Chemistry of India Rubber.

As stated before, Budde determined the rubber gravimetrically by first dissolving it in carbon tetrachloride, filtering the solution through glass-wool and precipitating it from the filtrate with his bromination mixture (6 cc. of bromine and 1 gram of iodine in one liter of carbon tetrachloride). After standing for 24 hours, one-half volume of alcohol was added and it was allowed to stand until the precipitate had settled clearly. The supernatant liquid was poured through a weighed filter, the tetrabromide decanted with a mixture of carbon tetrachloride and alcohol, finally with alcohol alone in order to remove the excess of bromine. A number of serious objections were soon made to the method as proposed by Budde; several sources of error, influencing the results in opposite directions, were demonstrated. Fendler and Kuhn found during an exhaustive study of the solubility of rubber in various solvents that a considerable amount of rubber remains undissolved in tetrachloride; this would consequently be removed during the filtration required in Budde's method. While this fact would tend to render low results, other points are apt to increase the percentages found. It is next to impossible to wash the bromine out completely from the inner parts of the lumpy tetrabromide precipitate by mere decantation with carbon tetrachloride and alcohol. Protein and resin bromides, the solubility of which in alcohol and tetrachloride has been disputed, would also add to the weight of the precipitate; finally, claim was made by several investigators that bromine reacted with rubber not only additively but also by substitution, especially when allowed to remain a long time in contact with the rubber solution. Harries and Rimpel even claimed to have separated such a substitution product. Under the pressure of so many objections, Budde modified his method to a volumetric one. Instead of dissolving and filtering the solution in carbon tetrachloride he adds his bromination mixture to a mere swelling of the rubber in carbon tetrachloride, allowing it to react for but 6 hours. The precipitate is treated in the same way as before and the wash-liquors poured through a filter to collect any possible particles of tetrabromide which might be carried off. The bulk of the precipitate is re-dissolved in carbon

bisulfide and separated from this solution with gasoline. This treatment has the double effect of removing the free bromine more exhaustively and converting the precipitate into a stable crystallized form. The crystals are oxidized with nitric acid in the original vessel in which they were precipitated. A sufficient, measured amount of standard silver nitrate solution is added and the mixture gently heated. The nitric acid has to be replaced from time to time, and the manipulation continued until the bromine is all combined as silver bromide. The excess of silver nitrate is titrated back by Volhard's well known method with ammonium thiocyanate. The formula $C_{10}H_{16}Br_4$ forms the basis for the calculation of pure rubber, four bromines corresponding to one caoutchouc, $C_{10}H_{16}$. In applying the method it is preferable to extract the sample first with acetone and eventually with alcoholic potash to remove completely the resins which might prove a disturbing factor by forming insoluble bromine compounds. Spence has only recently demonstrated by his investigations on rubber-proteins and their behavior towards bromine that the amount of the latter added to the tetrabromide in Budde's method is too small to materially influence the final results, provided the tetrabromide is calculated from the amount of bromine contained in the precipitate. The same author observed a regular loss of bromine when oxidizing the tetrabromide with nitric acid as proposed by Budde, a fact which was confirmed by Hinrichsen and Kindscher. They therefore suggested to replace the oxidizing and titrating process by a combustion in a current of oxygen or fusion with sodium-potassium-carbonate and potassium-nitrate mixture. The fusion method has been improved and more fully described by Spence who obtained satisfactory results. Budde's method, therefore, gives in the case of raw rubber, even at its present stage a fair idea as to the amount of rubber contained in a given sample. A more difficult problem faces the chemist in the case of vulcanized goods. The question, "What reactions take place during the bromination?" becomes more complicated and the composition of the products is a matter of great uncertainty; the method is, therefore, practically valueless for the estimation of pure rubber in cured goods.

Attempts to solve this problem were made by two different investigators. Axelrod precipitated the tetrabromide from a solution in kerosene with Budde's bromination mixture. The precipitate was washed in the same way as by Budde, and dried at from 50 to 60° C.; after weighing, it was ignited and the ash deducted. By analyzing a number of compounds of known composition he established a factor for the calculation of pure rubber from the bromo-sulfo compound. A moment's thought will at once reveal that such a determination is hardly applicable for general use. All sulfur of vulcanization is included in the bromine precipitate, and, as the coefficient of vulcanization is subject to considerable variation, it follows necessarily that the composition of the bromo-sulfur compound of rubber will be just as variable. We have, considering the present lack of a proper theory of vulcanization, no means to judge what reactions take place and what compounds result when cured rubber is brominated. If the sulfur of vulcanization is combined chemically with the rubber molecule, there is, of course, no room left for an addition of bromine to the double linkages which are saturated with sulfur. Huebener took this question into consideration, and, by adopting the Weber-Ditmar theory of vulcanization, concluded the reaction product of bromine and vulcanized rubber consisted of three distinct compounds: tetrabromide, dibromo-monosulfide, and disulfide. For purposes of calculation it is necessary to consider only tetrabromide and disulfide because two molecules of dibromo-monosulfide are equal to one molecule of tetrabromide and one molecule of disulfide. Therefore, not only bromine but also sulfur of vulcanization has to be determined to find the equivalents for pure rubber. He proposed at the same time a somewhat simplified method, originally designed for hard rubber, which has the advantage of eliminating the often very troublesome and long proposition of dissolving the rubber. The sample is finely rasped and brominated with elementary bromine under water. The results obtained in our laboratory have been invariably high, as it seems practically impossible to free the precipitate from the excess of bromine by a simple washing with hot water. Of course I have to admit that we have not made an exhaustive study of the subject and therefore are not ready to condemn the method as valueless.

Even if all methods, as described before, have failed to be satisfactory to everybody and in every instance, their development marks a decided progress in rubber chemistry. It can be justly hoped that at a not too far distant time chemists will be able to submit such methods of analysis as will be acceptable to both the merchant and the manufacturer. The importance of this problem was recognized at the International Rubber Exhibition at London when for the first time the International Testing Committee met in full session to discuss the questions which should be settled by this body.

THE VOLATILE ACIDITY OF GUM TRAGACANTH COMPARED WITH THAT OF INDIAN GUM.

By W. O. Emery.

Received March 13, 1912.

NEED OF THE INVESTIGATION.

The primary object of this investigation was to devise additional methods for the detection of Indian gum when substituted for or in admixture with tragacanth. A study of the literature early led to the conviction that among the degradation products of these gums there must be one susceptible of quantitative isolation and sufficiently characteristic to serve as an indicator of the purity, and therefore of the quantity, of parent substance involved in its hydrolysis. Such an indicator was believed to be represented by acetic acid, already isolated from one Indian

gum and reported as being present in another. The hope was entertained that tragacanth, under like treatment, might fail to yield this acid, but as will presently appear, experiment proved otherwise.

As defined by the United States Pharmacopoeia, tragacanth is the "gummy exudation from *Astragalus gummifer* Labillardière, or from other species of Astragalus, family Leguminosae, appearing in ribbon-shaped bands varying in size and from 1 to 3 mm. thick, or in irregular pieces of the same, long and linear, straight or spirally twisted; externally whitish, marked by more or less pronounced longitudinal or eccentric lines or ridges; translucent, fracture, short, rough, rendered more easily pulverizable by a heat of 50° C. (122° F.)."

While it is possible that the products known to the trade as "Indian gum" and employed so extensively in this country may vary as to their origin, it appears reasonably certain that two gums at least are justly characterized by this term, namely those of *Sterculia urens* and *Cochlospermum, gossypium*, both of which find local application as substitutes for tragacanth. It is equally certain that none of the so-called Indian gum has its origin in any species of Astragalus. Most of the Indian gum reaching this country bears little or no resemblance to tragacanth. A careful comparison of the commodity with authentic samples obtained direct, both from London and from India, clearly indicates that it corresponds in all essential points to the gum of *Sterculia urens*. It occurs in irregular, striated, sometimes twisted, translucent, or transparent lumps, never in ribbon-shaped bands or leaves.

In view of such physical characteristics, successful adulteration or substitution of whole gum tragacanth with Indian gum is no easy matter, and yet the latter product is occasionally offered for sale in the bazaars of India as true tragacanth.[1] It is, however, the powdered form of tragacanth that presents to the sophisticator more alluring possibilities. Owing to its extended use in the arts as well as in medicine, coupled with a relatively high price for the better grades, adulteration with the cheaper Indian gum has within the past few years been of frequent occurrence; hence any method looking to the detection and estimation of such adulterant must be welcome to all desirous of obtaining pure powdered tragacanth.

CHEMICAL PROPERTIES OF GUM TRAGACANTH.

According to researches carried on by O'Sullivan,[2] tragacanth consists of starch granules, cellulose—that portion insoluble in boiling water, cold dilute acids, and alkalies—likewise water-soluble gum yielding a series of gum acids of the nature of geddic acid, bassorin, bassoric acid, nitrogenous and mineral matter. As the result of an investigation of tragacanth from various sources, Hilger and Dreyfus,[3] among other conclusions, found that this product differs not only as regards chemical constitution, but also with respect to the proportion of degradation products formed when subjected to hydrolysis. None of the investigators of tragacanth, however, has, to the writer's knowledge, ever considered the possibility of acetic or other volatile acid constituting one of the hydrolytic products of this gum, due perhaps to the fact that it is odorless and without acid reaction in aqueous suspension, conditions not obtaining in the case of the two Indian gums herein considered. The remarkable property possessed by the gums of *Sterculia urens* and *Cochlospermum gossypium* of developing an acetous odor when exposed to moist air has been commented on by various authors; in fact, an examination by Robinson[1] of the hydrolytic products obtained with the gum of *Cochlospermum gossypium* developed the fact that an amount of acetic acid was formed equivalent to 14.4 per cent. of the original gum.

When gum tragacanth is heated with an aqueous mineral acid, as phosphoric or sulphuric acids, and the products of such action subjected to steam distillation, an acid distillate is obtained from which acetic acid can readily be isolated in the form of its silver salt. The procedure employed is as follows:

Treat 20 grams of whole gum first in the cold with 200 cc. of distilled water and 10 cc. of sirupy phosphoric acid until completely swollen, then subject for several hours to the full heat of the steam bath, whereby the mass gradually becomes partially liquefied, then distil the product with steam and evaporate the distillate to dryness in the presence of barium carbonate. Treat the residue with a little hot water, filter, and distil the filtrate, amounting to about 30 cc., with steam after the addition of 5 cc. of sirupy phosphoric acid.

On treating the distillate with silver oxid and filtering, characteristic plate-like needles were obtained, which on ignition proved to be silver acetate, as is evidenced by the following analytical data: 0.2048 gram of substance gave 0.1321 gram of silver; calculation for $C_2H_3O_2Ag$ gave 64.65 per cent. of silver, 64.50 per cent. being found.

There can, therefore, be no doubt that acetic acid constitutes one of the degradation products of tragacanth when heated with mineral acids.

ESTIMATION OF ACETIC ACID

Quantitatively, the acetic acid or, rather, "volatile acidity,"[2] is estimated as follows:

Treat 1 gram of the whole or powdered sample in a 700 cc. round-bottomed flask, provided with a long neck, for several hours in the cold with 100 cc. of distilled water and 5 cc. of sirupy phosphoric acid until the gum is completely swollen. Boil gently two hours in connection with a reflux condenser, whereby a nearly clear, colorless solution is effected. A very small amount of cellulose substance will remain undissolved. Now subject the hydrolyzed product to slow distillation in a vigorous current of steam until the distillate amounts to 600 cc. and the acid residue to about 20 cc. This should not be driven too

[1] Zornig, *Arzneidrogen*, **1909**, p. 634.
[2] *J. Chem. Soc. Trans.*, **79**, 1164 (1901); *Proc.*, **1901**, p. 156.
[3] *Ber. d. chem. Ges.*, **33**, 1190 (1900).

[1] *J. Chem. Soc. Trans.* **89**, 1496 (1906).
[2] The term "volatile acidity," as used herein, is the number of cubic centimeters of tenth-normal potassium hydroxid required to neutralize the volatile acid or acids obtained by subjecting the products to the action of aqueous phosphoric acid on 1 gram of gum to distillation with steam.

tar. However, otherwise there may be danger of scorching the non-volatile, organic degradation products, with consequent possible contamination of the distillate. It has been found that a spray trap of the form shown in Fig. 1, if used in connection with the flask containing the hydrolyzed gum, is effective in preventing traces of phosphoric acid being carried over into the distillate. Titrate with tenth-normal potassium hydroxid in connection with 10 drops of phenolphthalein solution, finally boiling the liquid under examination until a faint pink color persists. Run a control on same amount of distillate obtained by a parallel operation, with omission of gum, but using like quantities of other ingredients and observing the same conditions as in the test.

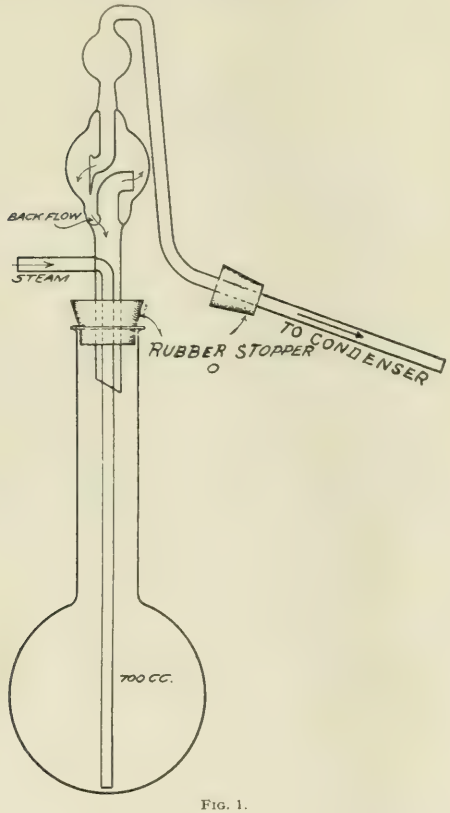


FIG. 1.

With a relatively large number of authentic gums (Turkey, Aleppo, and Persian), both whole and powdered, the following results were obtained:

Results on 35 samples of gum tragacanth, lump (cubic centimeters of tenth-normal potassium hydroxid): 3.9, 3.5, 4.2, 4.0, 3.4, 4.0, 3.2, 3.5, 4.0, 3.9, 3.4, 3.4, 3.6, 3.4, 3.5, 4.2, 4.0, 3.6, 3.3, 3.6, 3.8, 3.4, 3.3, 3.6, 3.4, 3.1, 3.3, 3.5, 3.4, 3.7, 3.4, 3.7, 3.7, 3.2, 3.4. These figures represent an average volatile acidity of 3.6 cc. Assuming this acidity to be due solely to acetic acid, it would be equivalent to 2.15 per cent. of acetic acid in the original gum.

Results on 21 samples of gum tragacanth, powdered (cc. tenth-normal potassium hydroxid): 3.8, 3.5, 3.5, 3.5, 3.6, 4.1, 3.8, 3.4, 3.9, 3.9, 3.7, 3.7, 3.8, 3.9, 3.6, 3.8, 3.6, 3.8, 3.5, 3.6, 3.8. This gives an average volatile acidity of 3.7 cc., equivalent to 2.20 per cent. of acetic acid in the original gum.

As regards the acetic acid content of Indian gum (*Cochlospermum gossypium*) it has already been shown by Robinson[1] to yield 14.4 per cent. of this acid. That of *Sterculia urens*, however, though early recorded by Guibourt[2] as emitting an acetous odor, has never before, to the writer's knowledge, been examined either as to the identity or the quantity of the acetic acid present. Five grams of Indian gum (*Sterculia urens*) were therefore treated in substantially the same manner as outlined for the isolation of the silver salt from the hydrolytic products of tragacanth. It may not be amiss to note in this connection that while tragacanth yields a practically colorless solution when boiled with aqueous phosphoric acid, Indian gum, on the other hand, gives a pink or rose-colored solution, a sure indication in an unknown sample that this product is present. The acid distillate obtained gave with silver oxid characteristic plate-like needles, which, on ignition, yielded values corresponding to silver acetate: 0.2010 gram of substance gave 0.1300 gram of silver; calculation for $C_2H_3O_2Ag$ gave 64.65 per cent., 64.67 per cent. being found.

Gram samples of whole and powdered Indian gum (*Sterculia urens*) were examined for volatile acidity, exactly as in the case of tragacanth, with the following results:

Results on 9 samples of Indian gum, lump (cc. tenth-normal potassium hydroxid): 26.3, 26.1, 26.6, 27.7, 27.1, 28.3, 25.9, 26.1, 26.8. These data indicate an average volatile acidity of 26.7 cc., corresponding to 15.91 per cent. of acetic acid in the original gum. The last of the nine samples, yielding 26.8 cc., was an authentic one obtained direct from the Indian Government; this acidity corresponds to 15.97 per cent. acetic acid.

Results of 14 samples of Indian gum, powdered (cc. tenth-normal potassium hydroxid): 26.5, 26.3, 26.1, 27.3, 26.3, 26.9, 25.4, 25.6, 27.7, 26.8, 26.6, 25.6, 27.6, 26.0. The average volatile acidity in this case is 26.5 cc., corresponding to 15.79 per cent. of acetic acid.

CONCLUSIONS.

From the foregoing data it appears that the volatile acidity or amount of volatile acid developed by gram samples of tragacanth, on the one hand, and Indian gum (*Sterculia urens*), on the other, is fairly constant, sufficiently so, indeed, to serve, in conjunction with other well-known tests, as a very reliable criterion for estimating the purity or quantity of either alone or in admixture. The volatile acidity of Indian gum (*Sterculia urens*) as compared with that of tragacanth is nearly 7.5 times as great.

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[1] *Loc. cit.*
[2] *Pharm. J.*, **15**, 57 (1855).

THE EXTRACTION OF POTASH AND ALUMINA FROM FELDSPAR.

By H. W. Foote and S. R. Scholes.

Received January 24, 1912.

Feldspar, being the only common American mineral containing potash in quantity, offers an interesting problem in its decomposition into salts of potassium and aluminium. The work that has been done on this problem has been reviewed by Cushman and Hubbard.[1] In their own work, these authors have considered the possibility of decomposing finely powdered feldspar by treatment with various reagents, particularly under the influence of the electric current. They found that hydrofluoric acid caused an amount of decomposition far above the theoretical, due to the hydrolysis of the fluorides by the action of the current, allowing the hydrofluoric acid to be used over and over again. For instance, in the direct action of hydrofluoric acid on the mineral, some potassium fluoride is formed, which hydrolyzes on electrolysis, and regenerates hydrofluoric acid at the anode. This acid is free to attack more feldspar, and the process goes on until the action is practically complete.

In some preliminary work (carried out several years ago by one of us with Mr. N. A. Martin), which was never published, it was found that at a temperature well above 100°, under pressure, hydrofluoric acid behaved as a catalytic agent in the presence of an aqueous solution of sulphuric acid, and considerable decomposition could be produced.

We have carried out a number of experiments, the results of which will be given below, and have found that under certain conditions decomposition is nearly complete. The hydrofluoric acid appears to be a catalytic agent in this case in the same sense that nitrogen tetroxide is a catalytic agent in the lead-chamber process for sulphuric acid; that is, to explain the action, it is necessary to assume that feldspar is attacked forming some intermediate compound, perhaps silicon fluoride, which hydrolyzes in the presence of water at a high temperature, regenerating hydrofluoric acid. Alumina and potash pass into solution at the same time, and can be recovered as sulphates.

In our experiments, we used a sample of very finely ground feldspar rock.

The material was analyzed by the ordinary methods, and found to have the following composition:

	Per. cent.
SiO_2	67.12
Al_2O_3	18.70
K_2O	10.84
Na_2O	3.12
CaO	0.46
H_2O	0.44
	100.68

The calcium fluoride used to produce hydrofluoric acid in solution had all passed a 200-mesh sieve.

The experiments were carried out in sealed glass tubes. The mixtures attacked the glass slightly at the temperatures used, but not sufficiently to affect the general results. After the heating, the contents of the bomb were treated with water to remove all soluble material and the solution transferred to a liter flask. Alumina was determined in an aliquot part, and from the result the percentage decomposition could be calculated. It was found by experiment that alumina could be determined in solution by direct precipitation with ammonia without first evaporating, since practically no silica was in solution. The results obtained are given in the table:

No.	Grams feldspar.	Grams CaF_2.	Grams H_2SO_4.	Grams H_2O.	Temp.	Hours heated.	Gram Al_2O_3 in $\frac{1}{10}$ aliquot.	Per cent. decomposed.
1	10	0.0	10	10	200°	23	0.0209	11.2
2	10	0.5	10	5	140°–150°	20	0.0723	38.7
3	10	0.5	10	20	140°–150°	20	0.1266	67.7
4	10	0.5	10	10	140°–150°	20	0.1362	72.8
5	10	0.5	10	10	140°–150°	40	0.1633	87.3
6	10	1.0	10	10	140°–150°	20	0.1662	88.9
7	10	1.0	10	10	100°	20	0.1355	72.4

If the fluoride, in the above experiments, were all used merely to form silicon fluoride or hydrofluosilicic acid, the decomposition would be much less in every experiment than what was actually found. In that case, the largest amount of fluoride used would attack only about six per cent. of the feldspar, which is very much less than the smallest amount of decomposition observed.

No. 1 shows the comparatively small effect produced by sulphuric acid alone, even at a much higher temperature than in the experiments where fluoride was used. Nos. 2, 3, and 4 show the effect of varying the dilution of the sulphuric acid, using the same amount of fluoride in each. Of the three dilutions tried, the fifty per cent. acid is the best for the purpose. No. 5 shows the diminishing speed of the reaction, as the time of treatment is increased. Comparing with No. 4, it seems that less than fifteen per cent. decomposition takes place in the second twenty hours. Increasing the amount of catalyzer has more effect as No. 6 shows, with nearly complete decomposition in twenty hours. Lower temperature very noticeably decreases the decomposition, as would be expected. No. 7 was identical in every respect with No. 6 except that the temperature was lower, and the amount decomposed fell from 88.9 to 72.4 per cent. It was found to be impracticable to heat the tubes containing fluoride much above 150°, as they invariably burst; so that we are unable to say at just what temperature decomposition would be practically complete within twenty hours.

Heating the mineral before it was treated in the closed tube has practically no effect. An experiment was carried out which duplicated No. 4 in every way except that the feldspar was heated to redness for a half-hour before being placed in the bomb with the reagents. The per cent. of decomposition was 70.7, a result nearly identical with No. 4.

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[1] *Jour. Am. Chem. Soc.*, **30**, 779 (1908).

A COLORIMETRIC METHOD FOR THE DETERMINATION OF CARBON IN IRON AND STEEL.

By Jerome F. Kohout

Received January 29, 1912

This method is similar to the one proposed by Eggert and may be used with Stead's modification. This method was worked out and used by the writer while engaged in iron and steel analysis, and is very useful in controlling the work of an open-hearth or similar furnace. It eliminates all necessity for calculation and gives direct readings which are accurate within the limits of colorimetric work.

The method consists in dissolving the sample and a standard iron or steel in dilute nitric acid (1–3) and comparing the colors. The essential difference lies in the method of dilution. In the old and ordinarily used way the sample is diluted to a definite volume, and the standard is then diluted until the color of both the solutions is the same. The carbon content of the sample is calculated from the ratio of the volumes of the two solutions. In the proposed method the standard is diluted to a definite volume depending on its carbon content, thus a standard of 0.5% carbon is diluted to 5 cc., one of 0.65% to 6.5 cc., etc. The sample is diluted until the colors match. The volume of the sample gives its carbon content directly without any calculation. Thus if the sample contained 6.8 cc. and matched a standard 6 cc. in volume, the carbon content of the sample was 0.68 per cent. C. It is always best to use a standard of about the same percentage of carbon as that of the sample so that the height of the two solutions will be about the same. The writer used tubes 7 mm. in diameter and graduated to 0.05 cc.; this gave greater height to the solution and allowed the volume to be read very closely. The weight of standard and sample taken was 0.1 gram each. In the following table the volumes given for the samples are the mean of several determinations run with each standard. In every case the colors matched when the sample was diluted to within 0.1 cc. of the amount given in the third column.

Standard.		Sample.		
Carbon det. by direct combustion in oxygen. Per cent.	Volume. cc.	Volume. cc.	Carbon. Per cent.	Carbon det. by direct combustion in oxygen. Per cent.
0.06	6.0	5.5	0.055	0.057
0.11	11.0	13.4	0.134	0.137
0.56	5.6	5.8	0.58	0.58
0.72	7.2	7.6	0.76	0.77
0.89	8.9	8.4	0.84	0.86
1.05	10.5	10.1	1.01	1.02

The results are very slightly lower than those obtained by direct combustion, but are close enough for routine commercial work and furnace control.

LABORATORY AND PLANT

THE DISTRIBUTION OF POWER IN PORTLAND CEMENT MANUFACTURE.[1]

By Richard K. Meade.

Received February 24, 1912.

In the manufacture of Portland cement, the question of power enters in quite largely. In the manufacture of 3,000 barrels of cement per day, there must be ground approximately 1,650 tons of material to an almost impalpable powder every twenty-four hours. Nine hundred tons of this represent the raw material which must be reduced from pieces of stone as large as a man can handle to such a degree of fineness that from 90 to 98 per cent. of the powder will pass a 100-mesh test sieve. Six hundred tons represent the slag-like clinker which must be pulverized so fine that at least 92 per cent. of it will pass this sieve, while the remaining one hundred and fifty tons consists of the coal for heating the kilns, which is pulverized to about the foregoing degree of fineness. The power required to run this amount of machinery is probably greater than that which would be utilized in the manufacture of a similar value of any other commodity.

In addition to running the machinery necessary for grinding, power is required in quarrying and transporting to the mill the raw materials, in operating the elevators and conveyors used to handle the product in the various stages of its manufacture, to revolve the kilns and to keep moving various minor operations of the process.

The size of the power plant which will be required in manufacturing 3,000 barrels of cement per day will depend largely upon the class of material to be ground, upon the type of machinery used to do this, and the degree to which it is done, as well as the proper installation of the plant itself and the means of transmitting the power to the machinery.

The general character of the power generators themselves and the arrangement of the engine and boiler rooms is similar to that of other manufacturing enterprises where much slow-moving, heavy machinery is operated. Cross compound condensing engines of the Corliss type are generally employed, although in electrically driven mills the steam turbine has been used successfully; when natural gas is available, gas engines are often employed.

The steam plant usually consists of water tube boilers. These are generally of the horizontal type, but, occasionally, vertical boilers are employed. At one or two mills the boilers are arranged to utilize the waste gases from the kilns in making steam, but this installation has never proved very satisfactory.

The transmission of power can be effected by either shaft or electrical drives, but, in either event, the distribution of the power to the mills must be effected with the least possible loss due to friction. When the transmission is non-electrical, short, powerful shafts

[1] Read at the meeting of the American Institute of Chemical Engineers at Washington, December, 1911.

are used which are driven by belting or rope drives, directly from the engines, and which in turn transmit the power to crushers and grinding mills.

In designing the power plant of a shaft-driven cement mill, it has usually been found best to run the mills grinding raw material with one engine and those grinding clinker by another, rather than to use one large engine for both. It has also been found best to run the kilns by a separate engine so that shut-downs may be avoided; and often here, too, the outlying machinery will be driven by means of a generator and motors.

The electrical transmission of power is now considered best for cement mills for a number of reasons: First, it permits of a better arrangement of the buildings, both as regards future extension and the bringing in of supplies. Second, as each machine is run by a separate motor, the plant is not affected by the shutting down of any particular machine and the operation is more continuous. Third, the steam turbine, a very economical prime mover, can be installed. Fourth, the upkeep on motors is less than on line shafts. Fifth, the economy under varying loads is greater. It is generally conceded, however, that where the mechanical transmission is a good one it is more economical of power, but the foregoing advantages are now considered to offset the greater steam economy of the mechanical system, which latter is seldom good. This is owing to the fact that an installation of Tube mills in a plant of any size requires much counter-shafting or else their being run with a bevel gear, while Fuller mills and Griffin mills require a quarter turn belt. For this reason the line shaft system is seldom placed at an advantage.

In the electrical system, the engines are connected direct or by belting to powerful alternating current electric generators and the current from these is carried about the mills by copper cables and distributed to motors which are directly connected sometimes by gearing but preferably by belting to the mills. Usually two or three engines of equal power are employed rather than one large one, on account of shut-downs. Where water power is at hand the generators are connected to powerful turbines and power thus very cheaply obtained.

One of the defects of mills actuated by horizontal alleys, such as the Fuller-Lehigh mill and the Griffin mill, has consisted in the necessity of driving them with a quarter twist belt. In the new plants employing these mills this has been done away with by the use of vertical motors. Practically all the newer mills have adopted the plan of driving their kilns and machinery in outlying buildings by means of individual motors, even where the rest of the plant is shaft driven. In such a plant about 25 per cent. of the power is transmitted electrically.

In the new plant of the Tidewater Portland Cement Co., Union Bridge, Md., not only the kilns, crushers and grinding machinery are motor-driven, but also the conveyors are so operated. Each conveyor and elevator has its *own* individual motor, doing away with practically all shafting in this mill.

Alternating current generators and motors are now almost universally employed in cement mills, as these are less effected by dust. The voltage employed is usually 500 to 600.

A few of the western plants have been able to make use of cheap hydrolytic power in their grinding. In practically all cases, the power has been purchased from some large outside corporation developing waterfalls. Among the mills at which this has been done may be mentioned the Santa Cruz Portland Cement Co. and the Cowell Portland Cement Co., both of California, and the Superior Portland Cement Co., of Baker, Washington. At some of the Kansas plants gas engines have been installed, using natural gas for power. These mills also use natural gas for burning.

At the new plants of the Universal Portland Cement Co., a subsidiary concern of the United States Steel Corporation, the waste gases from the blast furnace are used to generate the power required for cement manufacture. The gas engines are located at the furnace and are connected to generators. The power is transmitted some distance in each case to the cement mill. A separate motor is used for each machine.

Ordinarily, the actual amount of power required in the manufacture of Portland cement is considered at about 24 horse-power hours (or 1 h. p. day) per barrel of cement produced; or, in other words, to manufacture 3,000 barrels of cement per day 3,000 horse-power equipment will be needed. The actual quantity varies, as we have said, with the hardness of the raw materials and of the clinker and also with the engineering skill with which the plant is laid out with respect to power transmission.

At one of the newest of the electrically driven plants, recording Watt-meters have been installed in the various departments, and by means of these an accurate record is kept of the power employed in the various operations connected with the manufacture of a barrel of cement.

The figures so far obtained show the power to be distributed as follows:

	Per cent.
Air drills in the quarry	2.0
Transportation of the stone to the crushers	0.4
Limestone crushers	1.8
Shale crushers	0.1
Dryers	1.8
Raw ball mills	5.2
Raw Fuller mills	21.8
Kilns	5.9
Coal mill	4.2
Clinker ball mills	2.0
Clinker Fuller mills	43.2
Shipping and packing department	1.4
Loss, lights, etc	10.2

In the above table there is included in the power for each step that which is required to convey the material to the next. This accounts for the high percentage of power required by the kilns, as some of this power is utilized in conveying the clinker into a large clinker storage and bringing it out from this to the clinker mill.

In this plant, the raw materials consist of a soft limestone and shale. Gyratory crushers are used to reduce the material to sizes suitable for the ball mills,

and these latter are employed to prepare for the Fuller mills. Both the raw materials and the clinker are ground to a fineness of 96 per cent. passing a 100-mesh sieve. The clinker may be classed as difficult to pulverize, as it is always burned hard in order to secure high quality.

By referring to the table it will be seen that 30.7 per cent. of the power is required to prepare the material for the kilns and 45.2 per cent. for the pulverizing of the clinker. The other 24.1 per cent. is employed in the minor departments and represents also the losses in transmission lines, etc.

The distribution of the power among the various departments depends, of course, largely upon both the installation and the materials to be ground. From a ball and tube mill plant the following figures are obtainable:

	Per cent.
Crushers and dryers	5.6
Raw material pulverizing	29.8
Kilns	7.0
Finishing mills	39.6
Coal mill and miscellaneous	18.0

With very hard raw materials the power required to prepare these for the kilns has risen to 50 per cent. of the total power employed, but usually this department takes a little under one-third of the total power, and the clinker mill slightly more than this.

Roughly speaking, we should be able, on an average, to prepare material for the kilns at an expenditure of between 15 and 20 kw. h. per ton; or, from 5 to 7 kw. h. per barrel of cement produced. For the operation of the kilns and dryers, including the pulverizing of the coal for the former, about 2 kw. h. per barrel of cement should be sufficient, while, for the reduction of the clinker to cement, a final 7 to 10 kw. h. will be required, or, in all, from 14 to 19 kw. h. (or 0.78 to 1.06 h. p. day) per barrel. Rating a kw. h. as equivalent to about 3 pounds of ordinary steam coal (40,000 B. t. u.), a barrel of cement would represent from 42 to 57 pounds of coal for power and from 80 to 100 pounds for burning, or from 122 to 157 pounds in all.

The question has been raised as to the advantage of employing the wet process for burning, thereby securing a more easily ground clinker. It is also claimed that the wet process allows the raw materials to be more easily ground. The wet process, however, increases the fuel required for burning at least one-third, or 30 pounds at the lowest. As this quantity of coal is usually rated in practice as about equivalent to 10 kw. h., or almost as much power as is required to grind both the raw materials and the clinker, the wet process on the score of power economy at any rate does not seem to promise much.

A careful analysis of the power question, particularly where fuel is cheap, would seem to indicate that it is much more important to consider grinding machinery with a view to repairs and attendance than with a view to saving of horse-power. Of course, all things being equal, the saving of horse-power is essential, but in choosing machinery, economy of upkeep is fully as important as economy of power. One kw. h. will usually cost about half a cent to generate and will often cover the range of power per barrel between the various types of well-known pulverizers used in the cement industry. It may not, however, cover the difference in cost of repairs, etc. An analysis of the cost sheets of most cement plants will show that the cost of attendance and repairs in the raw and clinker grinding departments is fully as high as the cost of the power delivered to them. For example:

Operating labor	2.55	
Repairs	2.44	
Supplies	0.04	
		5.03
Power		3.09
Total		8.12

Indeed, the cost sheets of the average cement mill will show repairs to be a larger item than power. A good example of this is the following:

	Per bbl.
Operating labor	$0.20
Repairs	0.10
Kiln coal	0.103
Power	0.82
Packing	0.034
Office, laboratory, etc.	0.016
	$0.535

This data is taken from the books of a highly successful new mill and the figure obtained is only achieved by very careful and efficient management. The figures for power and repairs may both be considered low and serve well to show the relative relation between the two items.

In selecting the type of machinery to be installed in a cement plant, therefore, it is not sufficient to consider merely the relative power consumed by the different types per barrel of the product obtained, but also the repairs. The mechanical engineer has often shown a tendency to make selections based solely on power-efficiency tests made in the machinery manufacturers' experimental plant, only to find out on actual operation that the cost of repairs more than offset any saving in the coal bill.

NEW FORMS OF APPARATUS FOR GAS ANALYSIS.[1]

By F. M. Williams.

Received February 15, 1912.

Probably the best known and most widely used apparatus for gas analysis is that of Orsat, or one of its many modified forms. The numerous modifications which have appeared from time to time bespeak a high tribute to the general utility of this instrument and also a keen desire to remedy its shortcomings.

The faults in the original Orsat apparatus may be briefly summarized as follows:

First. Although portable, it is much too bulky. I find its size may be reduced nearly fifty per cent., still retaining the 100 cc. measuring burette and without impairing accuracy at any other point.

Second. It is awkward in manipulation, due to position of burette on the right-hand side, necessita-

[1] Paper presented at meeting of Division of Industrial Chemists and Chemical Engineers, Washington, December, 1911.

ting either left-handed manipulation or crossing the hands in the line of vision while operating.

Third. The design of its absorption pipettes with U-tube or goose-neck reservoir is particularly fragile and liable to breakage at the bend, with the attendant unpleasant deluge of highly concentrated caustic solutions.

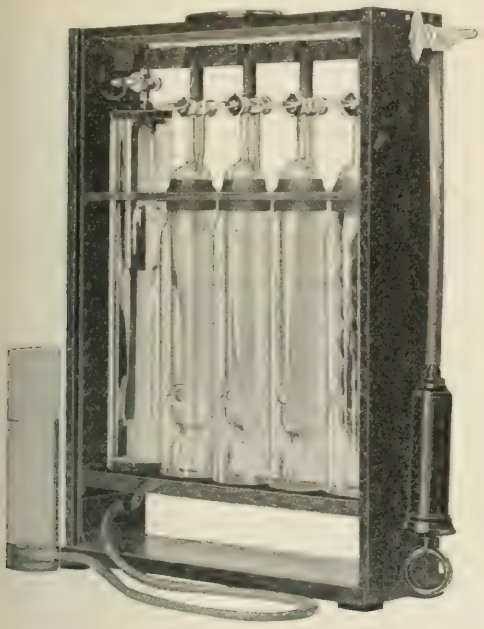

FIG. 1.

This form of pipette is difficult to wash and refill and is also slow in its absorption of gas.

In the modifications which are now submitted to your favorable consideration, the above noted objections have been overcome.

First. You will note a marked reduction in size. Model "A," arranged for the complete analysis of combustible gases, occupies a space of only 12 × 4 × 17½ inches, while the flue-gas apparatus, Model "B," is only 9½ × 4 × 17½ inches.

The measuring burette is placed at the left side, allowing freedom of the right hand in manipulating stopcocks, etc.

A special design of explosion burette is indicated in Fig. 2, with terminals permanently connected to binding-posts on outside of case. The bulb is placed lower upon the tube, permitting 15 cc. of clear graduation to be read on the small caliber of the burette above the swell.

The next point to be noted is the absorption pipette, of which two forms are shown, the simple and the bubbling, either form slipping interchangeably into the pipette jar or solution reservoir, with the closure at the top effected by an inexpensive rubber band.

Both forms are so constructed as to prevent the thin glass tubes from falling out when the pipette is removed from the jar.

The simple pipette needs little comment.

The bubbling pipette, which is exceedingly rapid in absorption, owes its high efficiency to the fact that the gas is not only caused to bubble through a long column of liquid but the bubbles are also finely broken up by the thin glass tubes with which the pipette is filled and a large absorption area is presented by the wet surface of these tubes.

While the arrangement at the top of this pipette somewhat resembles that of Babb, this difference is to be noted—in the original Babb the long capillary tube which passes to the bottom of the pipette enters at the center or highest point while in the form here presented the long tube enters at the side, allowing the short capillary, through which the liquid is brought up to the reference mark, to be placed at the highest point, thereby completely removing bubbles from the surface of the liquid.

The mounting of the glassware in the case is such as to render all parts accessible and instantly removable for cleaning or recharging. The T's at the top are held in a channel piece, *G*, resting in saddles. The front half of the cross-piece, *H*, is removable by lifting from the supporting saddles at the sides of the case.

The exposed portions of the inside of the case are rubber covered.

The detachable three-way T stopcock, with hard rubber pump and valves shown in Fig. 2, makes it possible to take a dry sample of gas directly from the source of supply, eliminating the inaccuracy and bother of collection over water, transference, etc.

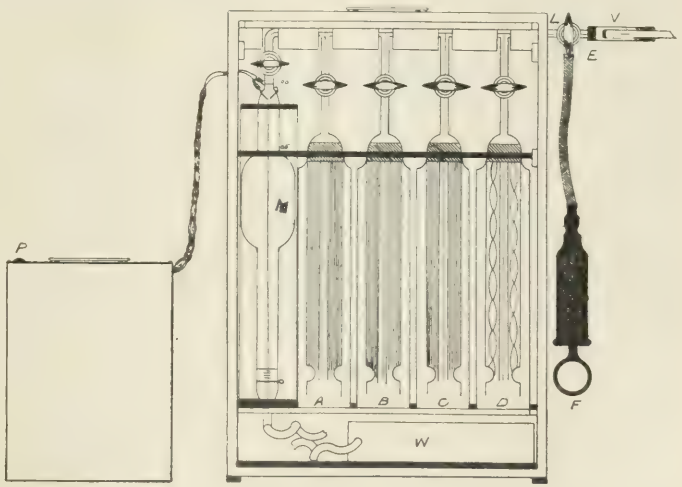

FIG. 2.—WILLIAMS IMPROVED GAS APPARATUS
MODEL A.
FOR COMPLETE ANALYSIS OF COMBUSTIBLE GAS—CARBON DIOXIDE, ILLUMINANTS, OXYGEN, CARBON MONOXIDE, HYDROGEN, METHANE AND NITROGEN.

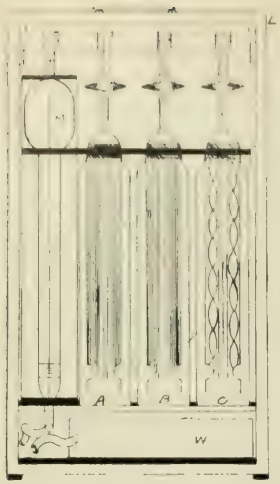

FIG. 3.—WILLIAMS' IMPROVED GAS APPARATUS, MODEL B. FOR ANALYSIS OF FLUE GAS—CARBON DIOXIDE, OXYGEN, CARBON MONOXIDE.

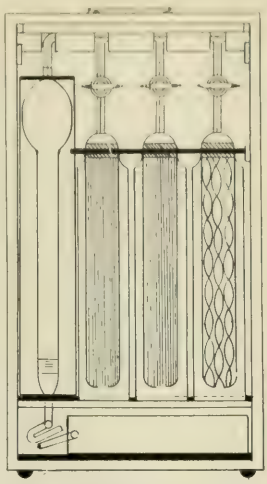

FIG. 4.—WILLIAMS' IMPROVED GAS APPARATUS, MODEL C. FOR ANALYSIS OF FLUE GAS—CARBON DIOXIDE, OXYGEN, CARBON MONOXIDE.

After connection with supply the pump is operated discarding the gas in the connecting line until the fresh sample is brought up to the apparatus, when by turning the stopcock and lowering the water-level bottle the measured sample is taken directly into the burette. This feature is especially advantageous in flue-gas analysis, when the apparatus may be permanently housed in the boiler-room with a line of piping running to the flues enabling an accurate determination of firing conditions to be quickly made at any time. The introduction of an aspirator tank into the line also enables an average sample to be taken covering any desired period of time. This method of control has some advantages, at least, over a recording CO_2 instrument, in that its accuracy and adjustment are unquestionable and we are also able to determine carbon monoxide, which is sometimes an important factor.

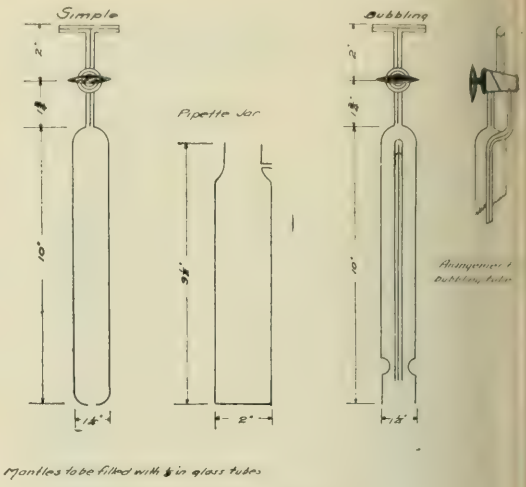

FIG. 5.—PIPETTE DETAILS.

In conclusion, the writer believes that years of experience with various kinds of gas apparatus warrants the statement that the form here described is without an equal in the combination of convenience, accuracy, rapidity and minimum liability to breakage.

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CURRENT INDUSTRIAL NEWS

By W. A. HAMOR.

TANNERY WASTES IN SEWAGE.

Gloversville, N. Y., the center of the glove industry in this country, has had a particularly trying experience with damage suits against tanneries located there, and under pressure of adverse verdicts, supported by an extensible injunction, the city has been obliged to adopt a new system of sewage disposal. In addition to the glove manufactories, Gloversville has 26 tanneries, at which glove leather and the finer grades of shoe leather are prepared. All of the domestic sewage, tannery waste (excluding hair) and mill refuse were formerly emptied directly into an adjoining creek, and it was by the riparian owners on this creek that the successful litigation was begun. The gross weight of wet and dry hides tanned annually in Gloversville amounts to 9,000,000 pounds, and about 8,000,000 pounds of chemicals are used in the tanning processes. The analyses of the creek water indicated that the quantity of wastes which found its way from the tanneries to the creek averaged over 30,000 pounds per day; and it has been estimated that fully one-half of the total weight of the hides and chemicals used in the processes of tanning was eventually conducted into the creek. The City Council of Gloversville passed an ordinance requiring all wastes from the tanneries to be passed through settling tanks before discharging into the intercepting sewer. Since this ruling, it is reported that if the tanks are kept properly cleaned, their efficiency is very satisfactory. The suspended matter occasionally exceeds 2,500 parts per million; but over 90 per cent. of the suspended matter is said to be removed in some cases, although the average is about 70 per cent.

The Gloversville situation is one of great importance to chemical manufacturers, and to tanners in particular, in view of the question of municipal power over nuisances in waters (see, in this connection, *L. R. A.*, **38,** 324; **39,** 649, 681). Sedimentation in large fields had been found to be unsatisfactory and expensive for the treatment of strawboard waste liquor, in which case the operators proceeded on a wrong principle (see *Water-Supply and Irrigation Paper No. 189, U. S. Geological Survey*, **1906,** p. 29). However, recent results at Gloversville seem to show that tannery wastes may be treated without resorting to mechanical filtration.

In 1901, a very important question arose in England as to whether the effluent from a tannery could be excluded from its sewage system by a rural district council on the ground that it caused a nuisance (Sevenoaks Rural District Council *v.* Whitmore, *Imp. Inst. J.*, July, 1901). The defendants had been called upon in 1886 to erect tanks on their premises in which the effluent from their works might settle before being pumped on to a sewage farm. They complied with this order, but their later refusal to cut off their connection as ordered led to the suit in 1901.

The defendants claimed that the nuisance was caused by unskilful management of the farm and that tannery effluents were as capable of bacterial treatment as sewage. A decision was rendered in favor of the defendants, on the ground that the sewage farm was ineffective.

A biological treatment of tannery effluents has also been proposed (Eitner, *Gerber*, **32**, 199, 213, 227).

Alsop [*Chem. Eng.*, **15**, 115 (1912)] has recently reported that the solids of tannery waste may be separated from the liquids by means of precipitating tanks, settling basins or centrifugal separators. He considers that the best plan is to use continuous centrifugal separators, which give control of the odors, and by means of which the solids can be placed in receptacles for incineration, for chemical treatment to recover ammonia, greases, etc., or for drying for use as fertilizers. The liquid waste, after the removal of the solids, is, according to Alsop's plan, run through ozone atomizers in a spray tower, falling on coke filters through which currents of ozonized air are continuously passing. It is said that the effluent resulting from this treatment is entirely unobjectionable from a sanitary standpoint, and that the cost of the treatment will in no case exceed, with all expenses of every kind, 10 cents per one thousand gallons of effluent.

SCIENTIFIC METHODS IN EARTHENWARE MANUFACTURE.

It has been said that the technology of the lower grades of pottery (common earthenware, Rockingham ware, majolica, faience, and stoneware) is comparatively simple; this is undoubtedly correct, viewing the earthenware industry as it exists to-day, but it is also true that less advantage has been taken of scientific methods and research in earthenware manufacture than in other industries. Harkort has recently discussed (*Z. angew. Chem.*, **24**, 2348) the composition of earthenware bodies and its relation to scientific results; it is from this contribution that the following material is taken.

The strength of earthenware is dependent, not as in porcelain on the fusion of the feldspar, but principally upon the close packing of the clay particles; it follows, therefore, that a determination of strength merely by the "ring" of the articles leaves out of account such factors as thickness, shape, etc. The value of earthenware depends, to a large extent, upon the flawless adhesion of the glaze, and as a defect may not become apparent for a considerable period, a rapid method of testing is important. Harkort heats the test-pieces in an electric oven, in which the temperature is gradually increased, and quenches them in water from different temperatures. His observations, extending for a year, have demonstrated that test-pieces which will stand higher temperatures withstand ordinary variations of temperatures longer; and that if no cracks are developed at a certain quenching temperature, a satisfactory deportment towards changes of temperature can be predicted. Seger attributed the formation of cracks and the splitting off of a glaze to a difference between the coefficients of expansion of the body and the glaze. Damaur made measurements on earthenware bodies and confirmed Seger's assumption; he showed that the coefficient of expansion increased with an increase in the silica content, but was affected by the temperature of firing, this is raised to the point of fusion. Harkort finds that silica lowers the expansion in glazes, but in sintered bodies the opposite effect is observed, since it retards the drawing together of the particles of clay substance; and that when the silica is fine-grained, the bodies are less liable to have glaze cracks. By means of his quenching process, definite limits have been found for the ratio of clay substance to silica in earthenware bodies. A certain amount of clay substance must be present to yield an easily workable body, but the silica content must be such that the coefficient of expansion represents an applicable value. It is pointed out that while finely ground silica must be added as sand is eliminated from well-washed clays, its addition has a tendency to weaken a body, and a high temperature of firing which would tend to strengthen would be disadvantageous from the point of view of the formation of glazed cracks, as the density developed promotes their formation. It is found that the larger the fire-shrinkage is, the smaller the coefficient of expansion, and the greater the sintering the larger the expansion. Additions of lime and feldspar increase the strength of the biscuit: the effect of the feldspar is attributable to its fusion, but at that temperature deformation results, although this is not observed when lime is added in amounts up to 20 per cent.; lime alone softens a body, and the burning temperature is slightly increased.

THE DECOLORIZATION OF SUGAR JUICE WITH "EPONITE."

In 1910, a substitute for animal charcoal in sugar refining was placed on the market by a Stockerau firm; this decolorizing substance, called "Eponite," is now being manufactured by two European companies, and is said to have received favorable consideration by some sugar refiners.

Eponite, as marketed, is a fine mealy powder, possessing a dull black color; it contains about 82 per cent. of carbon and 1.7 per cent. of ash, and seems to be of vegetable origin. Strohmer (*Oesterr.-Ungar. Z. Zuckerind.*, **39**, 687) conducted experiments which showed that it effected decolorization best on being heated with the sugar liquor for ten minutes at 80° C. with agitation, and that it had 10 times the decolorizing power of new char of fine grain and good quality. He found that whereas an ordinary refinery charcoal had no decolorizing action whatever on a 0.25 per cent. solution of saccharane, a definite chemical constituent of caramel (Ehrlich, *Bull. Assn. Chim. Sucr. et Dist.*, **27**, 140), eponite, under the same conditions, decreased the dark color of the solution by about 40 per cent. Further experiments by Strohmer demonstrated that its decolorizing power was not affected by the reaction of the solution; that it did not absorb sugar from concentrated solutions when heated for 10 minutes at 80° C.; and that it had a deodorizing action on impure sugar solutions, a property of some importance when working with beet liquors. He also pointed out that the very high decolorizing power of eponite would permit of smaller plant than is at present required for passing sugar liquors over charcoal, and that treatment in small tanks with the separation of the spent material by small filter-presses would appear feasible.

The experiments made by Prinsen-Geerligs (*Archief Suikerind. Nederl.-Ind.*, **19**, 1085), published more recently, indicate that eponite is hardly suitable for the decolorization of sugar juice in practice. From experiments on the *large* scale in the refinery, it was found by Prinsen-Geerligs that, taking the total cost of decolorizing with animal charcoal as 1.0, that with eponite is 1.7, and with another material, "Blankit," 2.0. Apart from the disadvantage of its comparatively high cost, he concluded that eponite is unsuitable for use because it passes to a greater or less extent through all filtering materials, owing to its very finely divided state. As a result, there appears in the juice or sirup a black turbidity which exerts a detrimental influence on the color of the finished product.

THE PREVENTION OF IRON AND STEEL CORROSION.

The Bradley process of rust-proofing iron and steel, as described by Brown (see *Eng. Min. J.*, **93**, No. 11, 538), consists in producing an unoxidizable coating on the surface of the metal. This is effected by heating the iron or steel objects in a muffle furnace heated with coal or coke. After introducing the objects into the furnace, the doors are sealed with brick to exclude air, and a jet of hydrogen is passed into the muffle to mingle with a stream of kerosene which is forced into the muffle under

pressure. The iron or steel objects become coated with a carbon and iron compound possessing a blue color when the objects are removed from the furnace; when cool, a thin coating of linseed oil is applied, changing the color to a deep black. The coating is said to resemble that produced by the Bower-Barff process in appearance, and to have a hardness of about 9.

A Pittsburgh manufacturing firm has for some time been making a special study of slow-corroding steel for pipe, and is reported to have succeeded in developing a soft steel having an exceptionally high degree of uniformity. This is said to have been further improved by a patented process of hot forging, known as *spellerizing*, which is applied to the metal in the course of manufacture, and which renders the surface more uniformly dense and less liable to become pitted. It is claimed that this steel will give good service in cases where no protective coating can be applied. To protect pipe from moisture, the same company has developed a coating to be applied to pipe ranging from 3 to 18½ inches in diameter.

The Coslettizing process, said to produce a black, rust-proof finish on iron, consists in boiling the article in a solution of 1 ounce of iron filings and 4 ounces of phosphoric acid in 1 gallon of water.

LOHMANNIZING.

The protection of iron and steel is at present effected by means of three zinc coating processes: the old "hot galvanizing" process, the "cold galvanizing" process (electrolytic zinc plating), and the "sherardizing" process (see *Met. Chem. Ind.*, **6**, 189; **10**, 253). The process of "Lohmannizing," invented by H. J. Lohmann, differs from these in that it is not restricted to the application of zinc coatings, but may, it is claimed, be used for coatings of zinc, lead, and tin in varying preparations to suit the requirements of each case.

The process of Lohmannizing begins, as usually, with pickling the iron and steel articles in a bath of sulphuric acid. Then the article is dipped into the Lohmann bath, which, being "composed of an acid and an amalgamated salt, further cleanses the pores and cavities, and deposits metallic salt upon the entire surface, penetrating into the most minute pores and cavities." The patent specification states that the Lohmann bath is a solution of hydrochloric acid, mercuric chloride, and ammonium chloride. Next follows drying and then immersion in the molten protective alloy which is at a temperature of 950 to 1000° F. "An amalgam or chemical union is thus formed between the amalgamating salt and the protective alloy." The temperature of the immersed article rises in contact with the molten alloy, and, when it reaches a temperature of 500°, volatilization of the mercury occurs. Since the mercury passes from the surface of the alloy, the complete surface is said to be left free and open for the protective alloy to fill its pores and cavities, there being freedom from oxidizing influences. As it is said that it is possible to obtain a perfectly satisfactory lead plating by the Lohmann process, it would seem that the process would be of value in the production of lead-lined apparatus.

THE INFLUENCE OF ADDITIONS TO BRONZE.

Bronze composed of copper and up to 20 per cent. of tin is usually specified for monumental work. It has been found, however, that the shrinkage of these pure copper-tin bronzes is considerable, and since it militates against the precise jointing of large bronze works of art cast in several pieces, undesirable experiences have been the result. Von Miller [*Metallurgie*, **9**, 63 (1912)], after experimenting on a bronze composed of 92 per cent. of copper and 8 per cent. of tin, has come to the following conclusions: Shrinkage can be appreciably diminished only by the addition of about 10 per cent. of zinc in the presence of tin. Cobalt, aluminium, silicon, iron, and nickel increase the shrinkage. Tensile strength is increased by cobalt, nickel and manganese, but is considerably lowered by antimony and zinc. Cutting, boring, chiseling and engraving are rendered easier by up to 2 per cent. of antimony and lead, and more difficult by nickel and manganese. The addition of tungsten, nickel, iron, manganese or cobalt raises the melting point. The formation of a patina is less on bronzes containing zinc and aluminium, but is greater on those containing cobalt, nickel, antimony, iron, silicon, or phosphorus than on a normal copper tin bronze. Patina formation was tested for with a weak solution of ammonium sulphydrate containing sulphur.

COPPER FUNGICIDES.

Pickering [*J. Agric. Sci.*, **4**, 273 (1912)] points out that the most effective form of Bordeaux mixture is obtained by adding lime water to copper sulphate until just short of alkalinity. This basic sulphate, which possesses the formula $10\,CuO.SO_3$ and is known as Woburn Bordeaux, has been shown by direct experiments to be equivalent to 6 times the weight of ordinary Bordeaux. According to Pickering, the copper in Bordeaux mixture is rendered soluble by the carbon dioxide, and dissolved copper is invariably present in the drip water collected from trees which have been sprayed. Gimingham and Barker (*J. Soc. Chem. Ind.*, **1911**, 760) have suggested that the solvent of the normally insoluble copper compound is a substance excreted by the fungus itself; but this is denied by Pickering and experiments are described to prove that the copper in Bordeaux mixture is brought into the soluble condition by the action of air. Pickering shows that the greater the excess of lime present the longer is the interval before this action commences; that Bordeaux mixture does not dissolve sufficiently to give a reaction for copper with ferrocyanide, although it does dissolve enough to react with iron; that an atmosphere of carbon dioxide greatly accelerates action, but until the carbon dioxide actually reaches a certain proportion a reduction of action is noticed; and that action is also increased by the presence of calcium sulphate. It would appear that if fungicidal action were dependent upon a solvent material exuded from the fungus, all basic sulphates and carbonates of copper would be equally efficacious for a given weight of copper present; but, as shown by Pickering, this is not the case.

THE UTILIZATION OF THE POTASSIUM CONTENT OF MINERALS.

Aschan [*Z. anorg. Chem.*, **74**, 55 (1912)] has recently investigated the utilization of the potassium contents of the "Rapakivi" and pegmatite granites. He has found that the potassium present in the feldspar may be rendered soluble in water by fusing the powder with anhydrous calcium chloride or with lime and sodium chloride (see, in this connection, Rhodin, *J. Soc. Chem. Ind.*, **1901**, 431), and both methods are considered of possible value in rendering the potassium available for agricultural purposes, the former presenting distinct advantages if the calcium chloride is obtainable cheaply. Aschan found that the greater part of the potassium in feldspar may also be rendered soluble, as hydroxide, by heating under pressure with lime and water. He found that treatment with acids was unsuitable.

PURIFICATION OF WATER BY FORCED OXIDATION.

It is reported that at Cardiff, Reading, Tunbridge Wells, and elsewhere in Great Britain, a new system of purifying water is in operation, and the results have, so far, been apparently satisfactory. The "Candy" apparatus consists of a steel cylinder, the lower portion of which contains the filtering media—fine silica grit, sand, and a special oxidizing substance termed "oxidium." A special correspondent of *Metallurgical and*

Chemical Engineering (10, No. 2, p. 86) reports that the water to be purified is forced into the cylinder at a pressure of from 5 lbs. to 25 lbs. per sq. in., depending upon the character of the water, and compresses the air in the upper portion thereof, thereby increasing to a considerable extent the amount of oxygen dissolved in the water; in cases of highly impure water, the air supply may be maintained at the necessary rate by the aid of a small force-pump. By this new apparatus it is said that oxidation of the dissolved iron compounds is so rapidly effected that the water leaves the filter practically free from iron. Organic matter also seems to be thoroughly removed. It is said that the cleansing of the filter may be easily conducted by reversing the flow of water, and it is stated that the quantity of water required for washing does not exceed 0.75 per cent. of the quantity filtered. A filter 8 ft. 3 in. in diameter is said to be capable of dealing with some 9,000 gal. per hour, and the capital cost of the apparatus is reported to be only from $15 to $20 per 1,000 gal. working capacity per day. Working expenses are put at $0.24 per 1,000,000 gal. for the "Candy" apparatus.

THE "CHLORIDE" WATER PURIFICATION PROCESS.

According to a patented process described by W. B. Bull (*Mun. Eng.*, **42**, 159), salt brine is electrolyzed in suitable cells; the resulting sodium hydroxide solution is concentrated and either sold or employed as a softening agent in the water supply; the chlorine gas produced is conducted into water, and the resulting chlorine water is passed upwards through a conical receptacle containing iron refuse, passing off therefrom as a ferric chloride solution, which is used in the same way as alum solution for the purification of water. Ferric chloride is said by Bull to replace alum at a fraction of the cost of the latter, and to be an improvement on the "iron and lime" process of purification.

THE SERPEK PROCESS OF NITROGEN FIXATION.

The Serpek process consists in heating bauxite with coal at a temperature of 1700° to 1800° C. It is said that 15 to 18 per cent. of nitrogen is absorbed as aluminum nitride. Treatment of the nitrogen-carrying bauxite with sodium hydroxide liberates ammonia, and it is claimed that the profit from the ammonia reduces the cost of alumina.

DIASTAFOR IN THE TEXTILE INDUSTRY.

Recent investigation has shown that diastase contains two enzymes capable of attacking starch. In 1906, Fraenkel and Hamburg separated, by dialysis, an enzyme which both liquefied and saccharified starch from one which only liquefied it, and further proved that diastase is not an albumin. Quite recently, Hamburg [see *J. Soc. Dyers and Col.*, **28**, 7–14 (1912)] has recommended "Diastafor" for use in textile industries as a uniform product. He has found that, for sizing yarns, farina converted by diastase easily penetrates the fiber, and for heavy sizes, the weighting material penetrates with it. In silk dyeing, increased strength and elasticity is given to the material. Hamburg states that "Diastafor" may be extensively used before bleaching operations for the removal of the sizing, the subsequent boiling operations in alkalies being in this way considerably shortened; this ensures greater preservation of the fiber and imparts a fuller handle to the goods. "Diastafor" is also used for degumming, since at low temperatures the color is not affected; for discharging when a half-bleach is required, or prior to mercerizing; and for the production of uniform finishes. "Diastafor-starch" finishes are said to penetrate the fiber evenly and to prevent the color from being saddened, thus producing very satisfactory results with regard to brightness, weight, handle, etc., of the goods.

WOOD PRESERVING.

At the Eighth Annual Convention of the Wood Preservers' Association, held in Chicago, H. F. Weiss pointed out the possibilities of conditioning wood with chemicals to change the appearance of a wood, such as beech to silverwood, and yellow birch to resemble black walnut, and stated that this process may have commercial value when the experimental stages are concluded.

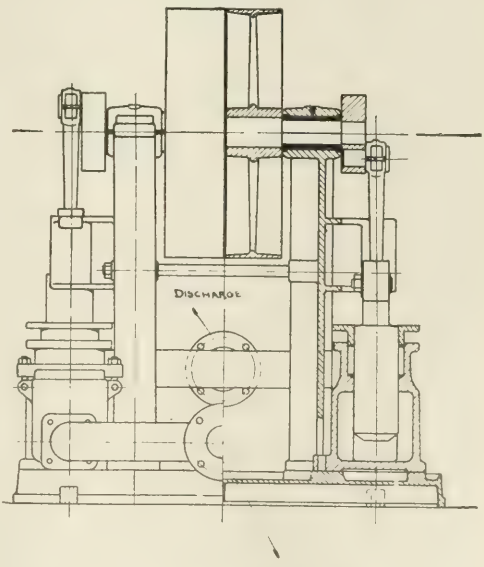
H. von Schrenk stated, in the course of a paper, that the heavier the oil the longer the life obtained; but pointed out that specifications calling for a density in creosote oil of 1.10 or more were impossible of attainment, for the heaviest oils known rarely exceed 1.082, and to make an oil with a specific gravity of 1.10 or more means that coal-tar pitch, etc., has to be added to creosote. It may be noted that the reason usually given for demanding a high density oil has been that such an oil would make the blocks more or less waterproof; but von Schrenk failed to find any marked evidence for this claim.

A NEW FILTERING MATERIAL FOR ALKALINE LIQUIDS.

In a recent patent (German Patent 241,710), the claim is for the use of "carbon-stones" as filtering material for acid and alkaline liquids. "Carbon-stones," which have been hitherto employed only for lining blast-furnaces, are prepared by grinding coke of low ash content, mixing it with about 20 per cent. of tar, compressing the mass in moulds, and then heating with exclusion of air. It is said that they can be used for the filtration of boiling concentrated solutions of potassium or sodium hydroxides.

PUMPS.

At one time pumps for only low pressure were manufactured, but the development of large chemical industries has rendered necessary extensive improvements in pump manufacturing industry, so that now there are pumps capable of handling corrosive acid and alkaline solutions, sewage and paper pulp,



PLAN OF A NEW STEAM PUMP.

and withstanding very high pressures. We have, moreover, reciprocating and centrifugal pumping machinery of various designs, elevator pumps, fire service pumps, geared pumps,

hydraulic transmission pumps, "hydropulsators," multi-stage high-lift centrifugals, screw pumps, turbine pumps, vacuum pumps, etc.

For use in connection with hydraulic forging presses, drawing benches, cartridge-case presses, etc., pumps are sometimes made which supply water at pressures of from 3000 to 6000 pounds per square inch. However, the capacity of such pumps rarely exceeds 10 or 15 gallons per minute. According to *Engineering News*, 67, 503, two pumps have been recently built by a Holyoke, Mass., company which are designed for a pressure of 5000 pounds per square inch with a capacity of 50 gallons per minute. These pumps are of the horizontal duplex type with outside-end-packed plungers, and each has four $2^1/_8$-inch diameter plungers with a common stroke of 18 inches.

The accompanying illustration shows a design which has recently come into use for pumping the black alkaline liquors used in pulp mills. This liquor is very corrosive to brass or bronze, but not, it is said, to "charcoal iron," and consequently the problem of design has been to make cylinders, plungers, and valves so that every part of the pump coming into contact with the liquor could be constructed of iron. In this new design, manufactured by a Buffalo company, this is claimed to have been accomplished. The plungers are guided mainly from cross-head, with short guide in the cylinder, the latter sufficient to keep the plungers in line without wearing the packing and causing a leaky pump. The passage of solid matter in suspension without clogging the valves, choking the waterways, or fouling the plunger, is said to have been accomplished by providing a low velocity of the liquid through the pump, by using large waterways and valve areas. Each valve has its separate, removable cover; and, under ordinary circumstances, no springs are used, the valves being of just the weight necessary to close without "slam."

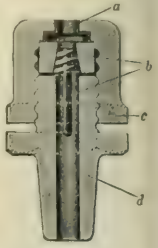
"RATISAL," A TRAP SUBSTITUTE.

A device intended to handle water of condensation, which has been given the name "Ratisal" by its inventor, H. C. Sommer, of Düsseldorf, Germany, consists of a tube-like conical shell containing a removable tube upon the external surface of which is formed a spiral screw. During normal operating conditions the valve attached to the device is closed and the water of condensation is thus forced to find an exit through the sinuous canal of gradually decreasing cross-section formed by the spiral screw and the inner surface of the shell. Since the canal is of considerable length, the frictional resistance offered to the passage of the water is almost equivalent to the pressure of the steam in the space being drained. By adjusting the sectional area of the canal, it is said that the frictional resistance may be regulated so that the water will have any desired pressure as it emerges from the device up to within a small degree of that of the steam. In order to accomplish this, two sizes of copper wire spirals are provided to wind into the screw to diminish the effective area. "Ratisal" is said to force the waste water through the drain pipe continuously and without loss of steam.

A DRY FIRE EXTINGUISHER FOR ELECTRIC INSTALLATIONS.

According to *Elektrotechnik und Maschinenbau*, 29, 581, tests were recently made on the "Elektra Trockenfeuerlöscher" in the Cologne municipal electric works. The apparatus, which is made by a Köln-Lindenthal manufacturer, is a slightly conical tube, 750 mm. long, charged with a white powder which liberates carbon dioxide when heated; the tube consists of an insulating material, 2 mm. thick. The powder is reported to have stood 50,000 volts alternating for five minutes when forming a bridge between terminals of the horn type. Arcs were extinguished by throwing the powder on them, and a fire built of wood soaked in petroleum, sending up flames close to two vertical bus-bars under 12,000 volts alternating, was extinguished without danger to the operators and without giving rise to strong current fluctuations.

A NEW PATTERN IN SPRAY NOZZLES.



A "new and improved" spray nozzle for sulphuric acid chambers is being manufactured by a London firm. These nozzles consist of a glass tip (*a*), embedded in the nozzle (*b*) by an acid-resisting putty, a lead casing (*c*), and a lead union (*d*). They are said to give a fine spray and to be capable of passing from 2 to 8 gallons per hour.

THE DIGBY AND BIGGS DIONIC WATER TESTER.

The fundamental idea in the "Dionic Water Tester" is to substitute a measurement of electrical conductivity for chemical analysis and to draw from the conductivity measurement conclusions as to the amount of impurities present in the water. It is said that the apparatus can be applied to measure hardness, leakage of cooling water into surface condensers, sewage pollution in rivers, minute traces of impurities in distilled water, the priming of steam boilers, etc. While this tester is not claimed to replace chemical water analysis in every case, it is said that it may be employed for purposes of control in large-scale practice.

NEW TANK VALVE.

A new type of valve for bottom outlets on tanks (German Patent 284,590) is made by a Halle a/S, Germany, firm. The valve stem is elongated so as to bring the valve seat close to the inside level of the tank and thus make a flush joint in the bottom of the tank (see Fig. 1). In this way it is said to be impossible for the outlet to become clogged by sediment or crystallization as is frequently the case where the valve is only a short distance from the tank. These valves are supplied to chemical manufacturers in iron, bronze, and in tin-, lead- and rubber-lined metal, and various types are available for either wood or metal tanks.

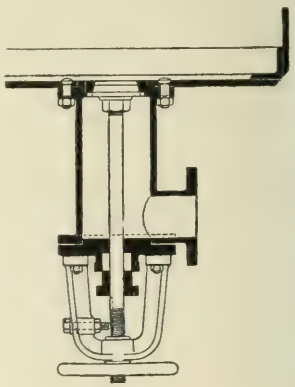


FIG. 1

NOTES AND CORRESPONDENCE

THE PAINT AND VARNISH INDUSTRY.

Editor of the Journal of Industrial and Engineering Chemistry:

A recent editorial, in THIS JOURNAL, on the condition of the paint and varnish industry appears to the writer to leave out of account certain important facts. In the first place, this industry, as a whole, is in a depressed state, due primarily to the advanced prices of materials. Repeated failures of crops of flaxseed have produced a high, and at the same time, fluctuating price for linseed oil, which, whatever may be the merits of the matter, is the only oil having popular confidence; China wood oil has special uses, but does not affect the price of linseed, and is, in fact, more costly; and there is a tendency the world over toward an increase in the price of lead and zinc, which are the bases of the only pigments that have any white color value. The turpentine dealers' corner which put up the price of that product last year undoubtedly caused many to begin using mineral substitutes, and this has been helped by the high price of everything else; but if oil becomes cheap again, which will probably occur sometime, the increased use for turpentine will send its price up; this will inevitably happen from the lessening supply in any case. The failure of the Navy Department to purchase seventy thousand dollars' worth could hardly have affected the market, as it is less than 1 per cent. of the amount exported—except that it has been used as an advertising item by the makers of substitutes. The same is true of the increased use of barytes and other cheap pigments by the Navy. The fact in regard to these is that the experts of the Bureau in charge of supplies have long complained that commanders of ships paint their vessels more often than is required for adequate protection; ten to fifty or more coats of paint are removed when a ship is repaired. This may be said to be a waste of paint; but the captains say that universal experience, both at home and on foreign ships, shows that a condition of absolute freshness and spotlessness is necessary for the maintenance of proper discipline, and the real use of paint is to keep the ship looking smart. Now the supply department says: "Very well, we will furnish as cheap a paint as possible that will look well when new; if it becomes brittle and scrapes off easily, so much the better." So they are doing as Mr. Toch says; and it is certainly a defensible position. It is not an economic problem at all; it is one of fighting efficiency. When it is a question of getting the most protective value for the money, as in painting the Capitol and other United States buildings at Washington, they are painted with straight corroded lead and linseed oil, exactly as they have been for a hundred years past.

Mineral oil substitutes for turpentine are much better than formerly; Chinese wood oil has made a strong and independent position for itself in the varnish business; but if linseed oil were to be sold at 50 cents per gallon, all the so-called substitutes for it would disappear. Such substitutes—not in all cases the same ones—were used more extensively twenty years ago than now; they will always be used to some extent. In limited proportions some of them have great value for special uses; but in a large way the present condition of this industry is affected by natural and general economic conditions far more than by changes of a merely technical character.

The tendency is constantly increasing to regard the unrestricted use of substitutes in the paint trade as a source of danger, and to more specifically define their legitimate uses; this, as in all other lines, involves contraction rather than expansion.

A. H. SABIN.

April 12th.

DETERMINATION OF MANGANESE IN STEEL.—A NOTE.

Editor of the Journal of Industrial and Engineering Chemistry:

In the March issue of THIS JOURNAL for the current year there appeared an article entitled "Determination of Manganese in Steel," by James J. Boyle.

The writer turned to this article in expectation of finding the description of a new method for the determination of this element, but after reading the method, was surprised that it should have been published in THIS JOURNAL, as it is essentially the same as published by Stehman in the *Journal of the American Chemical Society*, **24**, 1206 (1902), or ten years previously, and other points in the article were covered in my remarks on Stehman's method, Vol. **25**, 392 (1903).

Yours very truly,

H. E. WALTERS.

March 30, 1912.

1. APOCYNUM OR INDIAN HEMP, RUBBER.[1]

By CHARLES P. FOX.

Apocynum Hypercifolium (Nat. Order, Apocynaceae) is an indigenous plant common to many sections of the United States. It is a strong rooted perennial with reddish stem, fibrous bark, long, slender seed pods, seeds with long, white, cottony appendages, and a milky juice. The latex is white, viscous, neutral or slightly alkaline, and has the strong acrid odor peculiar to the plant.

The usual coagulating reagents react with this latex in the following manner:

Acids do not coagulate; latex becomes thin.

Alkalies do not coagulate; restore the viscosity; change the color from white to brownish yellow.

Boiling coagulates slightly; action slow.

Acetone ($^1/_{10}$ volume) coagulates immediately and completely; liquid is colored chocolate-red.

Formaldehyde coagulates readily but is much slower in action than acetone.

Phenol coagulates the latex, but gives a soft product.

Salt solution coagulates slowly, giving a finely divided precipitate hard to coalesce. *Boiling* the same solution gives a soft product.

Of the above methods, the use of alcohol or acetone, and formalin are the only ones recommended. Of these two, acetone is preferred.

The latex of *Apocynum* differs slightly from that of *Asclepias* in that it coagulates spontaneously, even if it is kept in closed containers.

The naturally coagulated latex gives:

	Per cent.
Liquid portion	67.58
Cheese (wet)	32.42

The *liquid* is white (not clear), slightly acid and with the characteristic acrid odor. This liquid failed to coagulate after addition of more acid. Slight excess of alkali increased its viscosity and changed its color from white to brownish yellow, but did not precipitate or coagulate it. Boiling had no effect. Excess of acetone gave a finely divided precipitate, the particles of which were not cohesive. Evaporation of the mixture, after washing with water and treatment with boiling acetone, gave a small quantity of a black, soft rubber destitute of strength.

The *cheese* was composed of:

[1] Presented before the Rubber Section, A. C. S., at forty-fifth meeting, Washington, December, 1911.

	Per cent.
Water	33.46
Rubber	3.99
Resin	62.98

Working up this *cheese* with solvents, removing foreign matter by filtering through gauze, evaporating, with low heat, the excess of solvent, adding an excess of precipitant, removing the precipitating agent, washing and drying the precipitate, gave a good grade rubber.

The rubber obtained in this manner was black, firm, not tacky, odorless and strong. In quantity, it is much better than the product obtained from its neighbor, milkweed.

Milkweed latex, however, is richer in rubber than that of Indian hemp. The amount of latex in the two plants are about the same. In both cases the amount of rubber present is too small to be of any economic importance.

Of the total rubber present in the latex, 96 per cent. of it is won in the cheese formed in the natural coagulation of the latex. Ninety-six per cent. of the total rubber found ranks as good grade rubber.

The *resin* is mahogany-red, transparent, medium hard, tasteless, with slight characteristic odor.

The soil conditions under which the plant was grown exerted an influence upon the amount of rubber in the latex. Plants grown on dry, sandy soil of West Akron, gave a latex containing 2.27 per cent. rubber and 20.69 per cent. resin. Latex from plants grown in the wet swamps of South Akron, contained only 1.12 per cent. rubber and 15.04 per cent. resin. Rubber from dry land plants appears to be of better quality than that obtained from wet grown plants.

Natural latex from dry grown plants, collected in August, during very dry weather, contained:

	Per cent.
Water	72.29
Solids	26.21
Ash	1.59

Rubber in fresh latex was 2.36 per cent.

AKRON, OHIO.

NATURAL GAS.

The Bureau of Mines has just issued Technical Paper No. 10, "Liquefied Products from Natural Gas; Their Properties and Uses," by Irving C. Allen, and George A. Burrell, in an effort to show how natural gas, which is being allowed to escape almost without restraint in almost all of the petroleum fields of the country, may be conserved.

By fractionating natural gas, either during or after liquefaction, four products can be commercially obtained: (1) The gaseous product, the common natural gas of commerce; (2) the semi-liquid product, known as the new "wild" product, which should be used only as a liquefied gas and should be held in high-pressure steel containers only; (3) the light liquid product, or light gasoline used for blending with heavy naphthas; and (4) the heavy liquid product, or ordinary high-grade gasoline.

The liquefaction of gases by pressure is not a new industry, but only recently has its application to natural gas been recognized as practicable.

Up to the last two years the general practice in the manufacture of liquid natural gas was to make the product by compression of the gas in single-stage compressors operated at a pressure of 150 to 300 pounds per square inch. The one product obtained, so-called "natural gasoline," was run into a tank and "weathered." The weathering consisted in allowing the lighter portions to volatilize spontaneously and escape into the open air until such time as the boiling away of the liquid had practically ceased. Thus the process involved a loss of 25 to 50 per cent., or even more. This loss was an absolute waste, not only of power and of cost of operating the engines and compressors but of the product itself.

The next step in the industry was to pass the waste gases (of which only the small quantity used for power had been utilized) from the single-stage compressor through a higher stage compressor, thereby getting a second and more volatile product a "wilder" liquid which was run back into the first and mixed with the first or heavier condensate. This mixture was then again weathered to a safe degree, whereby it lost the greater part of the more volatile product that had been condensed in the second stage.

Recently the process had been improved another step, in that the first stage compressor product is run into one tank and handled as ordinary gasoline; the second compressor product is run into a second tank and handled as a lighter gasoline, with which the heavy refinery naphthas can be enriched or enlivened.

The natural gas of this country frequently contains light products that do not condense in the second-stage compressor, and for which it is practicable and necessary to instal three, four, and even higher stage compressors. These light products —true gases at ordinary temperatures and pressures—can be compressed and liquefied, but the liquid gases so obtained must be handled as gases and not as oils.

NATURAL CEMENT VERSUS PORTLAND CEMENT.

The rise and fall of the natural cement industry in the United States is shown by Ernest F. Burchard, of the United States Geological Survey, in "The Cement Industry in 1910," recently issued by the Survey as an advance chapter of "Mineral Resources for 1910." A dozen years ago the production of natural cement was nearly 10,000,000 barrels; last year it was but 1,139,239 barrels.

PRODUCTION OF PORTLAND AND NATURAL CEMENT IN THE UNITED STATES, 1899–1910 (IN BARRELS).

Year.	Portland cement.	Natural cement.
1899	5,652,266	9,868,179
1901	12,711,225	7,084,823
1903	22,342,973	7,030,271
1905	35,246,812	4,473,149
1907	48,785,390	2,887,700
1909	64,991,431	1,537,638
1910	76,549,951	1,139,239

ELECTRIC PRODUCTION OF FERRO-TUNGSTEN.

The Ampère Co., of Berlin, now smelts scheelite direct with sulphide of iron, with an addition of carbon in the electric furnace, according to the *Mining Journal*. The sulphide of iron serves as a flux. The product is a ferro-tungsten, containing but little carbonate, in the form of uniformly smelted regulus. The reaction in this process is $CaWO_4 + FeS + 4C = FeW + CaS + 4CO$. The silica contained in the scheelite is fluxed by the addition of lime forming a fluid and easily removable slag in which is contained the calcium sulphide formed according to the reaction hereinbefore given.

BUREAU OF STANDARDS ANALYZED SAMPLES.

The Bureau of Standards, Washington, D. C., is now ready to distribute certain special steels, as follows: No. 30, Chrome-Vanadium; No. 32, Chrome-Nickel; No. 33, Nickel. The fee for these steels will be $2.50 each. A renewal of No. 19, Acid Open Hearth Steel, 0.2 carbon, will probably be ready before this notice appears in print. Until printed certificates can be had, the above steels will be issued with provisional certificates without details of analyses or descriptions of methods.

BOOK REVIEWS

"Rubber." By PHILIP SCHIDROWITZ, PH.D., F.C.S. Methuen & Company, Ltd., 36 Essex St., W. C., London. 1911. Pages xv + 303 + advertising 31. Price, $5.00.

This work is excellent and comprehensive. Chapter I, Historical, deals with the early knowledge and development of the rubber industry and a sketch of the development of the fundamental scientific ideas of rubber. Chaper II, The Production and Consumption of Rubber, contains a large number of figures giving production for various countries, together with a speculation as to the probable future production. Status of the rubber industry is shown by the tables of consumption of crude rubber for the United States, the United Kingdom, Germany and France. Chapter III, The General Nature of the Rubber Industry, is divided into three sections: 1st, Crude Rubber Industry; 2nd, Manufacturing Industry; 3rd, Waste Rubber Industry. To each of these, however, he gives but passing general notice. Chapter IV, Wild Rubber, discusses the four leading botanical orders of rubber-bearing species and gives very excellently the methods of preparation, the economic conditions of the tapping and collection of the latex, the various grades of commercial rubber, the general characteristics of the wild rubber and the differences due to their methods of preparation.

Chapter V discusses the Plantation Industry. The importance that the author ascribes to plantation rubber is seen by the amount of space in his book given to its discussion. Tables of approximate acreage under rubber, production per year, probable future productions, plantation yield, probable total production in 1916 and an extended discussion of the basic idea of the plantation industry in which the climate and locality suitable for planting, kind of land, nature of the soil, soil analyses, plantation methods, are discussed; also clearing, lining, facing, propagation, weeding, interplanting, tapping, the tapping age, tapping season, tapping methods, collection of the latex, treatment of the latex, coagulation of the latex, kind of coagulants used, including those both in more general use and experiments, washing of the rubber sheets, treatment of the scrap, the drying and curing, smoking and pressing, vacuum drying, color of plantation rubber—these subjects are all treated more or less fully. The future of the plantation industry is given considerable notice, including its advantages and disadvantages, the amounts invested in 1910, the quality of planted rubber, cost and productions, the question of labor, diseases and pests of the trees and competition from other sources. Chapter VI, The Preparation of Rubber other than Hevea on the Plantation System. Here the author deals with the methods of planting of the Ceara, the Castilloa, the Funtumia, the Fiscus, the Manihot, although not in the detail given to Ceylon.

Chapter VII, Industrial Rubber. The term "Industrial" is applied to those rubbers obtained from the Guayule shrub and the Jelutong tree. The author discusses the Production of Guayule Rubber from the shrub, conditions under which it grows and method of obtaining the rubber. The Jelutong rubber is dealt with in few pages, showing its method of coagulation and a description in general of the United Malaysian Rubber Company's works at Goebilt. This chapter closes with a description of rubber from vines.

In the foregoing three chapters 16 pages deal with wild rubber, 65 with plantation rubber and 8 with industrial rubber. In view of the fact that wild rubber is still the most important crude rubber in the market to-day, it would seem that rather too much emphasis is placed upon these divisions and leads one to believe that the point of view of the author in writing is rather a point of view of the future than of the present.

Chapter VIII, Rubber Latices and Coagulation, discusses briefly the chemical and physical properties of rubber latices, giving the chemical composition and brief summaries of the most modern works. Theories of coagulation and the influence of the method of coagulation on the quality are outlined. Chapter IX, Crude Rubbers Compared —"Tackiness." The author discusses the various theories which have been offered to account for "tackiness" in crude rubber.

Chapter X, The Chemistry of Crude Rubber. This is divided into two divisions: the chemistry of the pure hydrocarbon and the chemistry of the secondary constituents. Rubber resins, nitrogen in rubber, insoluble matter and composition of the rubber molecule, commercial synthetic rubber are mentioned as well as the derivatives of the rubber hydrocarbon. Considerable attention is given to the viscosity of rubber solutions. Chapter XI, The Theory of Vulcanization, deals with the theory of hot vulcanization and the theory of cold vulcanization.

Chapter XII, The Manufacture of Rubber Goods. The fundamental processes of rubber goods manufacture are described briefly. The description, however, centers around the English methods. This includes washing, drying and mixing, with the discussion of the various compounding ingredients, calendering, making up, vulcanizing, curing, cold vulcanization, spreading, and a very brief description of the manufacture of various rubber articles. Chapter XIII deals with substitutes and waste rubber disposal.

Chapter XIV deals with chemical, physical and mechanical properties of vulcanized rubber. Very little is stated about the chemical properties simply because very little is known, likewise, physical properties. Mechanical properties are discussed somewhat in detail, including extensions, compressions, and hysteresis. Chapter XV, The Chemical Analysis and Physical Examination of Rubber. The analysis of crude rubber, moisture, determination of resin, nitrogen, ash, insoluble matter and rubber are all discussed. The analysis of vulcanized rubber is also taken up according to Weber's method and physical tests and electrical tests are mentioned. Chapter XVI, Mechnical Tests. For tensile tests the author describes the method of making the test piece according to the ring method and discusses in detail the ring-shaped pieces, the machine of Schopper and the hysteresis machine. Compression tests, abrasion tests and hardness tests each have mention.

The appendix deals with contracts and specifications.

The book is replete with illustrations and references to the literature and is the most valuable book contribution to rubber literature that has been published in many years.

W. C. GEER.

Paint Technology and Tests. By HENRY A. GARDNER. 256 pages 6 × 9. $3.00. McGraw-Hill Book Co., New York.

This book is well printed and contains a large number of excellent illustrations. Its seventeen chapters, principally a compilation of the bulletins sent by Mr. Gardner, the Director of the Scientific Section of the Paint Manufacturers' Assn. of the United States, to its various members, contain a very large amount of excellent material and information.

Mr. Gardner himself has, for the past few years, devoted his entire attention to the scientific study of paint, and with a few exceptions his book is a valuable addition to the literature on the subject.

The writer cannot quite subscribe to some of the statements made as, for instance, the comparison between the strength of a paint film due to its three sizes as compared to the three sizes in cement concrete, nor should the steel fence tests be taken too seriously, in view of the fact that the addition of the so-called "inhibitives" has not by any means been proved.

Taking it all in all, Mr. Gardner has added greatly to the literature of paints, and his book should be in the laboratory of every paint manufacturer. MAXIMILIAN TOCH.

Chemicals, Oils and Paints. Glossary on Schedule A, Prepared under the Direction of the Tariff Board, Washington, D. C., 1912.

What is here entitled a Glossary on Schedule A, is more fully defined in the sub heading on the title page to be "An analysis by paragraphs of Schedule A of the tariff act of August 5th, 1909, and a statistical survey of the industries affected thereby with a comparison of tariff laws since 1883."

As is known, the constitution of the present Tariff Board authorizes them to gather information as to costs of production here and abroad of the articles which are the subject of tariff regulation and to furnish the same to the President when requested by him. It is not expected or allowed to make any suggestions as to modifications of tariff rates upon dutiable articles or upon any subject involving legislation, which is carefully reserved for Congress.

However, the Board has not only justified its existence and possibilities as an aid to legislation, but has gone far to create a healthful public sentiment in favor of non-partisan tariff enactment in the future based upon non-partisan study of economic conditions and comparisons between existing American and European manufacturing industries.

The first report of the Board was, as is remembered, upon Schedule K (Woolen Industry) and was conceded on all hands to have embodied a greater mass of importation than had ever been gathered before on this subject.

The present report on Chemicals, Oils and Paints, which constitue Schedule A of the Tariff act, is also, we venture to say, of positive value, as furnishing a fund of information not hitherto gathered for public use.

The work here presented has occupied Dr. Bernard Herstein, the chemical expert of the Tariff Board, several years in gathering and arranging for proper presentation. It has involved many visits to chemical works, the gathering of a library of special publications, governmental and otherwise, on the industries grouped together under this Schedule A, and selecting from these the information, both general and statistical, which we find in this volume.

The subject is handled in three sections, in the first of which each of the 83 paragraphs of Schedule A is commented upon, the nature of the article or class explained, and the process of manufacture connected therewith outlined; in the second of which, the chemical industry of the United States broadly is described both in its historical development and present conditions and illustrated by many statistical tables gathered from the census reports and the importation and exportation statistics currently published by the Government. The same is then done for the chief European countries and Canada. This section contains a mass of information gathered together in compact form which cannot but prove valuable for the chemical student as well as the economist and legislator.

In the third section recent Tariff laws covering Schedule A are reviewed and the rates under five different Tariff acts from 1883 to 1909 as affecting each of the 83 paragraphs of this schedule are tabulated for comparison and the free lists under each of these tariffs similarly compared in detail.

We think that this indication of the character of this publication and its scope will be sufficient to indicate its great value to the readers of THIS JOURNAL.

The careful study of this Glossary which the writer of this notice has had occasion to make, satisfies him that Dr. Herstein, the author and compiler, has given careful and conscientious work to it and has striven to be accurate and unbiased in his statement of facts. SAMUEL P. SADTLER.

Circular on Regulations for Illuminating Gas.

The National Bureau of Standards is about to issue a circular entitled "State and Municipal Regulations for the Quality, Distribution and Testing of Illuminating Gas." This circular (133 pages, uniform in style with other Bureau circulars) has been prepared after conference and correspondence with a large number of gas engineers and inspectors; and it represents, as nearly as possible, the average opinion of many men active in the field of gas manufacture and gas testing.

Part I of the circular gives a summary of the municipal gas ordinances now operative, presents a general discussion of municipal gas requirements, and proposes an ordinance largely compiled from the best ordinance requirements now in force.

Part II treats similarly of State control of gas companies and proposes technical rules for state regulations.

Part III quotes a few ordinances typical of those recently enacted and gives the main portions of state gas laws now in force affecting gas quality, pressure and meter accuracy.

The circular does not concern itself with financial regulation of gas companies nor does it include any discussion of the comparative value of various methods of works management. It deals mainly with the candlepower, heating value, purity and pressure of the gas and gas meter testing.

The present publication has grown out of the investigation of the methods and standards employed in gas photometry and gas colorimetry, undertaken by the Bureau three years ago. A second circular on the methods of testing employed for official inspection work is now being prepared. Although it cannot be expected that the regulations for our methods of gas testing will ever be entirely uniform throughout the country, it is believed that if the results of a comprehensive investigation of the subject are published, a greater uniformity of method, and in some cases more accurate measurements, will result.

The attitude of the Bureau of Standards is entirely advisory and its intention is to place in the hands of the technical and general public an impartial and, as nearly as may be, an accurate summary of the facts which must be considered in connection with the fixing of standards of quality and the testing of illuminating gas.

Revision of the circular from time to time is contemplated in order to amend the recommendations as to the requirements to adapt it to new developments in the gas industry.

The circular is now in press and will be ready for distribution soon after April 1st. Copies may be obtained free of charge by addressing The Director, Bureau of Standards, Washington, D. C.

Metallurgy of Iron and Steel. By BRADLEY STOUGHTON, PH.B B.S. 2nd Ed. 8vo. 307 illustrations, i to xii + 537 pp Price, $3.00. McGraw-Hill Book Co., Publishers, New York City.

The author is already known to the students of Metallurgy in Iron and Steel by reason of his many years of untiring labor in this particular field, and the first edition of his book which appeared in 1908.

The first position held by the author after leaving college was that of metallurgist for the Illinois Steel Co., at South Chicago where he obtained practical experience. Later he was Adjunct Professor of Metallurgy, Columbia University, New York City. In this work he obtained much valuable information and education by contact with the well known metallurgist, Prof. I

M. Howe, to whom the book is affectionately dedicated. At present he is a Consulting Engineer, making a specialty of the manufacture of iron and steel. The practical and theoretical knowledge thus acquired especially qualifies the author to write a systematic, logical and highly accurate book on the subject. He has carefully examined all the best authorities, quoted them freely, and taken especial pains to give the authors quoted due credit.

In the preface, the author very aptly states that developments in the metallurgy of iron and steel have been so rapid during the past three years that it was not only desirable but necessary to thoroughly revise and in some cases rewrite entire sections for this edition. The theory and chemistry of the Bessemer and Open-Hearth processes have been rewritten and enlarged, as well as the whole chapter on Malleable Cast Iron. Such extensive changes have been made in all the text that the type has been reset from cover to cover. A very notable and agreeable change is that of placing the references to literature in an Appendix at the end of the volume instead of at the end of each chapter, as in the first edition. Facts relative to basic principles of the subject are very accurately stated and set forth in a clear and comprehensive manner. The different processes of manufacture are precisely described, the latest practice given, keen observations and comparisons made in regard to the effect of impurities and their removal in the finished product, and conclusions are logically drawn. Theories are very carefully introduced throughout the book, and the different lines of reasoning given, supporting the various theories advanced.

The author definitely expresses his own opinion where the facts merit it, but where conclusive evidence is lacking, in support of a theory, he says: "Statements must necessarily be made tentatively, with the idea of presenting the facts so that they may be of some practical benefit, even though later information may oblige us to change slightly the scientific basis on which we found them." The above indicates the attitude of the author in his effort to present the latest and best on the subject and this attitude is apparent throughout the entire book.

Space forbids, in a review of this nature, pointing out all the salient features of this book. It is replete with tables giving analyses of the various raw materials used, the metals produced from them, and their accompanying slags. The many figures and diagrams presented are very valuable aids to a thorough understanding of the subject. The book is well written, is the best of its kind to date, and will command respect. It is a pleasure to review a book of this nature, and it is earnestly recommended to those who are seeking accurate information on this important subject.

The author is to be heartily congratulated in this, his latest achievement.

The usual good workmanship of the publisher is apparent, and the book is remarkably free from typographical errors.

WILLIAM BRADY.

Casein, Its Preparation and Technical Utilization. By ROBERT SCHERER. Translated from the German by Chas. Salter. (Second Enlarged English Edition.) 173 pp., 11 illustrations. D. Van Nostrand Co., New York. Price, $3.00.

The uses of casein except for food purposes is a subject little known to the chemist, manufacturer and public, and the second enlarged English edition of "Casein" will be welcomed by all interested in the uses of casein and casein products.

The general arrangement and text is excellent and is very similar to the 1906 edition. There are several typographical errors, none of which however, interfere with a proper understanding of the text. The book is arranged in twelve chapters and an appendix giving recent patents granted for the improved manufacture and utilization of casein.

Chapter 1. Introduction.
Chapter 2. Casein: Its Origin, Preparation and Properties.
Chapter 3. Various Methods of Preparing Casein.
Chapter 4. Composition and Properties of Casein.
Chapter 5. Casein Paints.
Chapter 6. The Technics of Casein Painting.
Chapter 7. Casein Adhesives and Putties.
Chapter 8. The Preparation of Plastic Masses.
Chapter 9. Uses of Casein in the Textile Industry, for Finishing, Color Printing, etc.
Chapter 10. Casein Foodstuffs.
Chapter 11. Sundry Applications of Casein.
Chapter 12. Casein Compounds.

The subject matter is well arranged and gives the preparation and formulas of the casein compounds used for foodstuffs and technical purposes, and thus brings together the scattered literature on casein and many of its little known applications.

O. KRESS.

NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian, Chemists' Club, New York.

Analysis; Fundamentals of Qualitative . By V. THOMAS AND D. GAUTHIER. 8vo., 326 pp. $2.00. Gauthier-Villars, Paris. (French.)

Analysis; Gas and Fuel— for Engineers. By AUGUSTUS H. GILL. 6th Ed. 12mo., 139 pp. $1.25. John Wiley & Sons, New York.

Analysis; Manual of Chemical—. (Translation.) By E. PROST. Roy 8vo., 300 pp. $4.50. Oil & Color Trades Journal, London.

Analysis; The Methods of Volumetric—. (Mohr's Titriermethode.) By H. BECKURTS. 8th Ed. L. 8vo., 483 pp. $2.50. F. Vieweg & Sohn, Brunswick. (German.)

Analysis; Technical Methods of Chemical—. Vol. II. (Translation.) By GEORGE LUNGE. Vol. II. New Ed. 8vo., 1294 pp. $18.00. D. Van Nostrand Co., New York.

Areometry; Handbook of—. By J. DOMKE AND E. REIMERDES. 8vo., 247 pp. $3.25. Julius Springer, Berlin. (German.)

Coal; Methods of Analyzing— and Coke. By FREDERIC M. STANTON AND ARNO C. FIELDNER. 8vo., 21 pp. U. S. Bureau of Mines, Technical Paper 8.

Coals; Steaming Tests of— and Related Investigations. By L. P. BRECKENRIDGE, HENRY KREISINGER AND WALTER T. RAY. 8vo., 380 pp. U. S. Bureau of Mines, Bulletin 23.

Cocoa and Chocolate; Their Chemistry and Manufacture. By R. WHYMPER. $3.75. J. A. Churchill, London.

Coloring; Organic— Matter. Parts 2 and 3. By GUSTAV SCHULTZ. 5th Ed. 4, 80 pp. $1.50. Weidmannsche Buchhandlung, Berlin. (German.)

Crucibles, Making Porcelain and Silica—, etc. By P. A. YODER. 8vo., 3 pp. U. S. Dept. of Agriculture, Bureau of Chemistry, Circular 93.

Dyes; The Sulfur—; Their Production and Use. By O. LANGE. L. 8vo., 497 pp. $6.00. O. Spamer, Leipzig. (German.)

Electrochemical Process of the Chemical Manufacturing Industries. Vol. II. By JEAN BILLITER. L. 8vo., 514 pp. $6.75. Wilhelm Knapp, Halle. (German.)

Evaporation, Condensing and Cooling. By E. HAUSBRAND. 5th Ed. 8vo., 480 pp. Julius Springer, Berlin. (German.)

Explosives; Historical Papers on Modern—. By GEORGE

W. MacDonald. 8vo., 188 pp. $2.00. Whittaker & Co., New York.

Fuel; An Introduction to the Study of—. By F. J. Brislee 8vo., 258 pp. $2.25. Constable & Co., London.

Furnace; The Electric Vacuum— and its Use. By O. Goecke. Thesis; Technical High School, Danzig. (German.)

Gas; Liquefied Products from Natural—; Their Properties and Uses. By Irving C. Allen and George H. Burrell. 8vo. U. S. Bureau of Mines, Technical Paper No. 10.

Gas; Theory and Practice of the— Manufacturing Industry. Vol. I, Part 1. By Rudolf Mewes. L. 8vo., 403 pp. $4.50. H. A. Ludwig Degener, Leipzig. (German.)

Hydraulics; Treatise on . By Mansfield Merriman. 9th Ed. 8vo., 565 pp. $4.00. John Wiley & Sons, New York.

Inorganic; Groundwork of— Chemistry. By Wilhelm Ostwald. 3d Ed. 8vo., 860 pp. $4.50. Wilhelm Engelmann, Leipzig. (German.)

Management; Applied Methods of Scientific—. By Frederic A. Parkhurst. 8vo., 325 pp. $2.00. John Wiley & Sons, New York.

Materials; Laboratory Manual for Testing— of Construction. By L. A. Waterbury. 12mo., 270 pp. $1.50. John Wiley & Sons, New York.

Mercerization; The Technic of—. By E. Herzinger. 8vo., 254 pp. $1.50. M. Koch, Leipzig. (German.)

Oils, Modification of the Herzfeld-Bohme Method for the Detection of Mineral Oil in other—. By F. P. Veitch and Marion G. Donk. 8vo. U. S. Dept. of Agriculture, Bureau of Chemistry, Circular 85.

Oil, Per cent. Tables for— in Cottonseed Products. By Charles H. Herty. 8vo., 50 pp. University Press, Chapel Hill, N. C.

Pharmaceutical, Textbook of— Chemistry. By E. Schmidt. Vol. II. L. 8vo., 3562 pp. $7.25. F. Vieweg & Sohn, Brunswick. (German.)

Potassium; Handbook of the— Mines, Wells, etc. Anon. $3.00. Kuten Zeitung, Berlin. (German.)

Powder; Manufacture of Nitro-Lignin and Sporting—. By Earle Durnford. 8vo., 84 pp. $1.25. Whittaker & Co., New York.

Rubber; Cultivation and Preparation of Para—. By W. H. Johnson. 2d Ed. 8vo. $2.00. Maclaren & Sons, London.

Resins; The Distillation of—. (Translation.) By N. Schweizer. Demy 8vo., 185 pp. $2.00. Oil & Color Trades Journal, London.

Rubber and Gutta-percha. By W. R. Dunstan. 8vo., 440 pp. Imperial Institute, Colonial Report 82.

Rubber; Hevea Brasiliensis or Para—. By Herbert Wright. New Ed. Roy 8vo., 680 pp. $4.50. Maclaren & Sons, London.

Silk; Artificial—: Its Production, Qualities and Use. By K. Suevern. 3d Ed. 8vo., $4.50. Julius Springer, Berlin. (German.)

Sirup, Sorghum— Manufacture. A. Hugh Bryan. 8vo., 40 pp. U. S. Dept. of Agriculture, Farmers' Bulletin 477.

Spearmint, A Chemical Investigation of American— Oil. By E. K. Nelson. 8vo., 4 pp. U. S. Dept. of Agriculture, Bureau of Chemistry, Circular 92.

Stamp Milling. By Algernon Del Mar. 8vo., 134 pp. $2.00. McGraw-Hill Book Co., New York.

Steel; Its Metallurgy and Mechanical Treatment. By W. Roberts-Austen. Vol. II. 4th Ed. 8vo., 959 pp. $12.00. D. Van Nostrand Co., New York.

Sugar; Stohmann's Handbook of— Manufacture. A. Schauder. New Ed. 8vo., $6.50. Paul Parey, Berlin. (German.)

Temperatures; The Measurement of—. By G. K. Burgess and H. Le Chatelier. 3rd Ed. 8vo., 510 pp. $4.00. John Wiley & Sons, New York.

Textile; The Use of Fatty Substances and of Products Derived therefrom in the— Industry. By F. Erbau. L. 8vo., 365 pp. $4.75. W. Knapp, Halle. (German.)

Varnish; German Making. (Translation.) By Max Bottler. L. 12mo., 363 pp. $3.50. John Wiley & Sons, New York.

Water Analysis. By Herbert B. Stocks. Cr. 8vo. $1.25. Charles Griffin & Co., London.

RECENT JOURNAL ARTICLES OF INTEREST TO THE INDUSTRIAL CHEMIST.

Conveyors, A Study of Mechanical—. II. By Lincoln De G. Moss. *School of Mines Quarterly*, Vol. 33, 1912, No. 3, pp. 233–258.

Corrosion; The Effect of Various Substances on the Rate of — of Iron by Sulfuric Acid. (Advance Copy.) By Oliver P. Watts. *Transactions American Electrochemical Society*, Vol. 21, 1912, No. 23, p. 17.

Fibers, A Study of Linen—. By Hans Wrede. *Paper*, Vol. 6, 1912, No. 12, pp. 15–17, 36.

Furnaces; Gas Circulation in Electrical Reduction—. (Advance Copy.) By Jos. W. Richards. *Transactions American Electrochemical Society*, Vol. 21, 1912, No. 18, p. 5.

Gas; Recent Developments in the Manufacture of Water—. By Viggo E. Bird. *Progressive Age*, Vol. 30, 1912, No. 6, pp. 244–249.

Malting; Some Aspects of Floor—. By Thomas R. Dixon. *Journal of the Institute of Brewing*, Vol. 18, 1912, No. 2, pp. 105–126.

Nitrogen; An Unrecognized Source of Error in the Kjeldahl-Gunning Method for the Determination of—. By P. A. W Self. *Pharmaceutical Journal*, Vol. 88, 1912, No. 2527, pp. 384–385.

Paper, Progress of the Chemistry of— Making. By Arthur D. Little. *Paper*, Vol. 6, 1912, No. 10, pp. 25–28.

Patents. By William H. Davis. *School of Mines Quarterly* Vol. 33, 1912, No. 3, pp. 209–228.

Permanganate; The Standardization of Potassium— Solution by Sodium Oxalate. By R. S. McBride. *Journal of the American Chemical Society*, Vol. 34, 1912, No. 4, pp. 393–416

Precipitation; The Electrical— of Suspended Particles. By F. G. Cottrell. *Cement and Engineering News*, Vol. 24, 1912, No. 4, pp. 99–104.

Producer Gas; Recent Improvements in— Appliances. By Walter O. Amsler. *Industrial World*, Vol. 46, 1912, No. 12, pp. 342–345.

Pumping by Compressed Air. By Herbert T. Abrams. *School of Mines Quarterly*, Vol. 33, 1912, No. 3, pp. 293–311.

Spices. By Henry A. Ridley. 8vo., 449 pp. $2.25. Macmillan Co., New York.

Sucrose, The Determination of— in Cane Molasses by the Double Polarization Method Using Invertase and Acid as Hydrolysts By James P. Ogilvie. *International Sugar Journal*, Vol. 14, 1912, No. 158, pp. 89–93.

Sugar; Contribution to our Knowledge of Multiple Evaporation By Ed. Koppeschaar. *International Sugar Journal*, Vol. 14, 1912, No. 159, pp. 149–154.

Tars, Coke-Oven— of the United States. By Prévost Hubbard. 8vo., 11 pp. U. S. Dept. of Agriculture, Office of Public Roads, Circular 97.

Textiles; Fibrous and Spinable Substances in 1911. By W. Massot. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 12, pp. 562–574.

Textiles, The Danger Accompanying the Use of Magnesium Chloride in Finishing—. By E. Ristenpart. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 7, pp. 289–292.

Turpentine; The Production of Formic and Acetic Acids by the Atmospheric Oxidation of—. By C. T. Kingzett and R. C. Woodcock. *Journal of the Society of Chemical Industry*, Vol. 31, 1912, No. 6, pp. 265–268.

Water, The Influence of Mineral Constituents of— in Brewing By G. H. Gemmel. *Journal of the Institute of Brewing*, Vol. 18, 1912, No. 1, pp. 34–47.

RECENT INVENTIONS

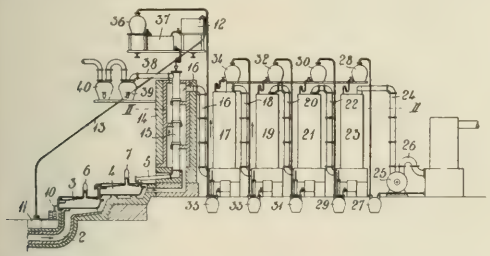
Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

PROCESS OF CONCENTRATING NITRIC ACID.

U. S. Patent No. 1,009,197, to Ragnar Sohlman, of Bofors, and Carl Olof Lundholm, of Ardeer, Scotland.

This invention relates to a process for producing from the acid of 25 to 40 per cent. produced by well known methods, a concentrated acid of 90 to 97 per cent. such as is generally used for industrial purposes, the said process rendering it possible to utilize the heat of hot gases, and being, therefore, suitable for use in connection with the production of nitric acid by the electric oxidation of nitrogen of the air.

The process consists in making a preliminary concentration of nitric acid by direct contact with a current of hot gases,

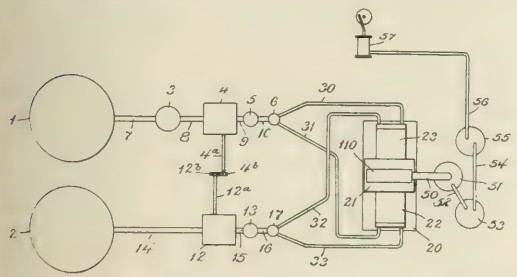


mixing the nitric acid thus concentrated with concentrated sulfuric acid, and distilling the nitric acid from the mixture and then concentrating the sulfuric acid for re-use in the process, one and the same current of hot gases being successively utilized for concentrating the dilute sulfuric acid, for distilling strong nitric acid from the mixture of nitric and sulfuric acids, and for preconcentrating the weak nitric acid by direct contact with the hot gases.

APPARATUS FOR PRODUCING CHLORIDS OF CARBON.

U. S. Patent No. 1,009,428, to James MacKaye, of Cambridge, Massachusetts. Assignor to Stone and Webster.

This is an apparatus for producing chlorides of carbon, comprising a reaction chamber with branches, the walls being of material which will resist cold chlorine, said chamber and its branches being filled with a porous corrosion resisting material,

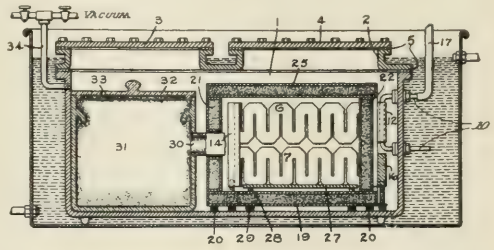


a lining adapted to resist hot chlorine in the main body of the chamber within the walls, and heating means within said lined part of the chamber, a liquid cooling circulation about the branches of the chamber, inlets for chlorine and methane at one end of the branches of the chamber, and means for supplying the gases in the proper proportions to said branches and mixing them therein in the presence of the porous medium before they are permitted to react, and an outlet for the products of the reaction, and means for collecting and retaining the same.

ELECTRIC FURNACE.

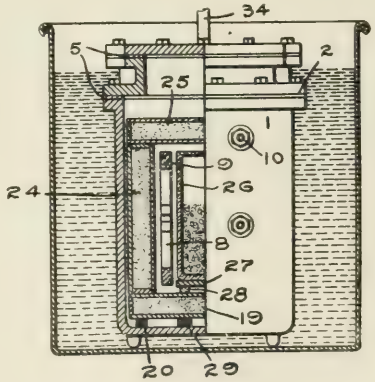
U. S. Patent No. 1,009,625, to William C. Arsem, of Schenectady, New York, Assignor to General Electric Company.

This invention comprises an electric furnace having a heating chamber and a condensing chamber, and having various ele-



ments so constructed and arranged that metals or compounds may be vaporized in the hot zone and then condensed in the cooler zone. According to this invention, the whole operation of vaporizing and condensing can be carried out in a vacuum or in a suitable gas or gases.

The invention comprises a furnace, the combination of a metal envelope, water-cooled terminals passing through said



envelope and insulated therefrom, a heater connected with said terminals and consisting of a plurality of grids connected in series and forming a rectangular space for the reception of a crucible to be heated, and a heat-reflecting screen consisting of graphite boxes packed with refractory powder and enclosing said grids to concentrate the heating effect on the crucible and its charge.

MARKET REPORT.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF APRIL.

ORGANIC CHEMICALS.

Acetanilid	Lb.	20½	@	23
Acetone (drums)	Lb.	15	@	16½
Alcohol, grain (188 proof)	Gal.	2.56	@	2.58
Alcohol, wood (95 per cent.)	Gal.	50	@	52
Alcohol, denatured (180 proof	Gal.	40	@	42
Amyl Acetate	Gal.	2.90	@	3.00
Acetic Acid (28 per cent.)	C.	1.87½	@	2.02½
Aniline Oil	Lb.	10¾	@	11½
Benzoic Acid	Lb.	23½	@	28
Carbon Tetrachloride (drums)	Lb.	10½	@	15
Carbon Bisulphide	Lb.	nominal		
Chloroform	Lb.	20	@	30
Carbolic Acid (drums)	Lb.	16	@	18
Citric Acid (domestic), crystals	Lb.	38½	@	39
Camphor (refined in bulk)	Lb.	—	@	44
Dextrine (imported potato)	Lb.	5½	@	5¾
Dextrine (corn)	C.	3.20	@	3.56
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	17½	@	20
Oxalic Acid	Lb.	7¾	@	8
Pyrogallic Acid (bulk)	Lb.	1.35	@	1.45
Salicylic Acid	Lb.	32	@	34
Starch (corn)	C.	2.45	@	2.75
Starch (potato)	Lb.	5	@	5¼
Tannic Acid (commercial)	Lb.	35	@	35½
Tartaric Acid, crystals	Lb.	30½	@	31

INORGANIC CHEMICALS.

Acetate of Lime (gray)	C.	2.25	@	2.30
Acetate of Lead (brown, broken)	Lb	7¾	@	8
Alum (lump)	C.	1.75	@	2.00
Ammonium Carbonate, domestic	Lb.	8	@	8¼
Ammonium Chloride, gray	Lb.	6⅛	@	6¼
Aluminum Sulphate	C.	90	@	1.75
Aqua Ammonia (drums) 16°	Lb.	2¼	@	2½
Arsenic, white	Lb.	3¾	@	3⅞
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Barium Chloride	C.	1.40	@	1.55
Barium Nitrate	Lb.	4¾	@	5
Borax, crystals (bags)	Lb.	3½	@	4
Boric Acid, crystals (powd.)	Lb.	7	@	7½
Bromine, bulk	Lb.	25	@	30
Bleaching Powder (35 per cent.)	C.	1.20	@	1.30
Barytes (prime white, foreign)	Ton	18.50	@	22.50
Blue Vitriol	Lb.	5½	@	5¾
Calcium Chloride	C.	65	@	90
Chalk (light precipitated)	Lb.	4½	@	6
China Clay (imported)	Ton	11.50	@	18.00
Feldspar	Ton	7.00	@	9.00
Fuller's Earth, powdered	C.	80	@	85
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1.15	@	1.55
Iodine (resublimed)	Lb.	2.60	@	2.65
Lead Nitrate	Lb.	8⅛	@	8⅝
Lithium Carbonate	Lb.	67	@	70
Magnesite (raw)	Ton	7.50	@	8.50
Nitric Acid, 36°	Lb.	3⅞	@	4¼
Phosphorus	Lb.	35	@	90
Phosphoric Acid, sp. gr. 1.75	Lb.	22	@	26
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bromide	Lb.	31	@	34
Potassium Permanganate (bulk)	Lb.	9¼	@	10
Potassium Cyanide (bulk) 98–99 per cent	Lb.	19½	@	21
Potassium Iodide (bulk)	Lb.	2.10	@	2.15
Potassium Chlorate, crystals	Lb.	8¼	@	9½
Potassium Nitrate (crude)	Lb.	4¾	@	5
Potassium Bichromate, 50°	Lb.	6⅞	@	7
Quicksilver	Flask	41.00	@	43.00
Salt Cake (glass-makers')	C.	55	@	65
Silver Nitrate	Oz.	36⅞	@	38⅞
Soapstone in bags	Ton	10.00	@	12.00
Sodium Acetate	Lb.	4¼	@	5
Sodium Chlorate	Lb.	8¼	@	9½
Sodium Bicarbonate (English)	Lb.	2¾	@	3
Sodium Bichromate	Lb.	5	@	5¼
Sodium Hydroxide, 60 per cent.	C.	1.70	@	1.75
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent., spot	C.	2.35	@	2.45
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	6⅞	@	7⅝
Sulphur, Roll	C.	1.85	@	2.15
Sulphur, Flowers (sublimed)	C.	2.20	@	2.60
Sulphuric Acid, 60° B.	C.	85	@	1.00
Talc (American)	Ton	15.00	@	20.00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	12¾	@	13
Tin Oxide	Lb.	47	@	51
Zinc Chloride (granulated)	Lb.	4½	@	5
Zinc Sulphate	Lb.	2¼	@	2½

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	40	@	45
Black Mineral Oil, 29 gravity	Gal.	12	@	12½
Castor Oil (No. 3)	Lb.	9½	@	10½
Ceresin (yellow)	Lb.	9	@	15
Corn Oil	C.	5.60	@	5.70
Cottonseed Oil (crude), f. o. b. mill	Gal.	40	@	—
Cylinder Oil (light, filtered)	Gal.	19½	@	20
Japan Wax	Lb.	9¼	@	9½
Lard Oil (prime winter)	Gal.	80	@	85
Linseed Oil (double-boiled)	Gal.	75	@	78
Paraffine Oil (high viscosity)	Gal.	23½	@	24
Paraffine (crude 120 & 122 m. p.)	Lb.	3	@	3⅛
Rosin Oil (first run)	Gal.	38	@	40
Spindle Oil, No. 1	Gal.	14	@	14½
Sperm Oil (bleached winter) 38°	Gal.	74	@	76
Stearic Acid (double-pressed)	Lb.	9	@	10
Tallow (acidless)	Gal.	60	@	63
Tar Oil (distilled)	Gal.	30	@	31

METALS.

Aluminum (No. 1 ingots)	Lb.	20	@	20½
Antimony (Hallet's)	Lb.	7¾	@	8
Bismuth (New York)	Lb.	2.10	@	2.15
Copper (electrolytic)	Lb.	16	@	16⅛
Copper (lake)	Lb.	16.05	@	—
Lead, N. Y	Lb.	4.22½	@	—
Nickel	Lb.	40	@	45
Platinum (refined)	Oz.	45.50	@	46.00
Silver	Oz.	59⅜	@	—
Tin	Lb.	43¾	@	44
Zinc	Lb.	6.85	@	—

FERTILIZER MATERIALS.

Ammonium Sulphate	C.	3.40	@	3.45
Fish Scrap, domestic, dried	Unit	2.90	@	10
Blood, dried	Unit	2.85	@	—
Tankage, high grade	Unit	2.70	@	10
Bone, 4½ & 50, ground, raw	Ton	27.00	@	—
Potassium, "muriate," basis 80 per cent.	Ton	38.55	@	—
Phosphate, acid, 16 per cent.	Ton	7.50	@	7.75
Phosphate rock; f. o. b. mine:				
Florida land pebble 68 per cent.	Ton	3.70	@	3.80
Tennessee, 68–72 per cent.	Ton	4.25	@	4.50
Pyrites, furnace size, imported	Unit	0.13½	@	—
Castor meal	Unit	nominal		
Mowrah meal	Ton	8.50	@	9.00

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume IV | JUNE, 1912 | No. 6

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Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly. Foreign postage seventy-five cents, Canada, Cuba and Mexico excepted.

Entered at the Post-Office, Easton, Pa., as Second-class Matter

ESCHENBACH PRINTING COMPANY, EASTON, PENNA.

TABLE OF CONTENTS

EDITORIALS:
- The Scope of Pharmaceutical Chemistry 396

ORIGINAL PAPERS:
- Structure of Galvanized Iron. By Walter Arthur and William H. Walker 397
- The Estimation of Oxygen and Occluded Gases in Copper and a Correction to the Electrolytic Assay in The Complete Analysis of Copper. By George L. Heath 402
- Some Observations on the Disintegration of Cinder Concrete. By George Borrowman 405
- The Manufacture of Chloroform from Bleaching Powder and Ethyl Alcohol. By F. W. Frerichs 406
- Comparison of Some Methods for the Estimation of Sulfur in Vulcanized Rubber with Especial Reference to Electrolytic Oxidation. By D. Spence and J. Young 413
- A Method for Determining the Value of Commercial Starches for Use in Cotton Mills. By G. M. MacNider 417
- The Chemistry of Anaesthetics, IV: Chloroform. By Charles Baskerville and W. A. Hamor 422
- Some Data on the Manufacture of Smoking Opium and Its Chemical Composition. By A. B. Adams and James M. Doran 429
- The Composition of the Pacific Kelps. By J. W. Turrentine 431
- A Note on the Determination of Iodides by Direct Titration. By J. W. Turrentine 435
- Determination of Total Potassium in Minerals. By Charles J. Schollenberger 436
- Note on the Neutral Permanganate Method for the Availability of Organic Nitrogen. By John Phillips Street 437
- Activity of Organic Nitrogen as Measured by the Alkaline Permanganate Method. By C. H. Jones 438
- The Effect of the "Wet Process" on the Availability of Low-Grade Nitrogenous Materials. By Burt L. Hartwell and F. R. Pember 441
- Neutral Ammonium Citrate Solution. By A. J. Patten and C. S. Robinson 443

LABORATORY AND PLANT:
- The Manufacture of Gelatine. By Ludwig A. Thiele 446
- A Punch for Straight Rubber Test Pieces. By Harry P. Mills 452
- A Laboratory Generator for Hydrochloric Acid Gas. By Edwin Dowzard 452
- Two Pieces of Laboratory Apparatus. By Harold Canning Chapin 453
- Unique Water Bath. By S. W. Wiley 454

ADDRESSES:
- Occupational Poisoning in Chemical Trades. By W. Gilman Thompson 454
- The Progress of the Work on the Revision of the United States Pharmacopoeia. By J. P. Remington 457

CURRENT INDUSTRIAL NEWS:
- The Industrial Uses of Ozone 459
- Non-Freezing Mixtures 460
- A New Liquid Mixer 460
- The Sterilization of Potable Waters 461
- Portland Cement 461
- Bleaching Powder as a Soap Substitute 461
- Water-Gauge Glasses 461
- Packing in Steam Plants 461
- Developments in Steam Generation 462
- The Contact Process of Sulphuric Acid Manufacture 462
- Fortoline 462
- The Utilization of Storage Battery Sludge 462
- The Manufacture of White Lead 462
- The Purity of Commercial Metals 462
- The Cost of Chlorine 463
- Synthetic Organic Dyes and Patents for the Manufacture of the Same, 1907–'11 463
- The Manufacture of Aluminum Foil 463
- Some New "Non-Corrosive" Alloys 463
- Kupronizing 463

NOTES AND CORRESPONDENCE:
- The German Patent System 464
- Originality of Inventions 465
- Report of the Delegate to the Joint Conference on the Patent System 466
- Report of the Committee on Quantitative Methods 467
- The Technical Analysis of Brass and the Non-Ferrous Alloys: Author's Note 469
- Volatility of Metals of the Platinum Group 470
- Chemistry and the Lithographic Industry 470
- Contamination of Laboratory Samples by Iron Derived from Crushing Machinery 471
- Combating Miners' Diseases 471

BOOK REVIEWS:
- Strength of Materials; Fertilizer and Fertilizer Hints; Die Chemie der Cellulose with Particular Reference to the Textile and Cellulose Industries, Chemiker Kalender; The Manufacture of Varnishes, and Kindred Industries; Technical Methods of Chemical Analysis; Cocoa and Chocolate, Their Chemistry and Manufacture; A Manual of Fire Assaying 471

NEW PUBLICATIONS 474

RECENT INVENTIONS 475

MARKET REPORT 476

EDITORIALS

THE SCOPE OF PHARMACEUTICAL CHEMISTRY.

The term Pharmaceutical Chemistry conveys no very definite idea to many who are engaged in other branches of the science; and with these indeed, may be included many who are connected with this branch of chemistry. For this condition, the pharmaceutical chemists themselves are responsible. Men engaged in the various divisions of pharmaceutical work, forgetting how dependent they are upon the other classes of workers in this field, have failed to keep in touch with one another. With this condition existing among the pharmaceutical chemists it is not difficult to understand why other chemists often have vague ideas as to what pharmaceutical chemistry comprises.

The term should be applied to the chemistry directly involved in the preparation and dispensing of medicines, in other words, that connected with the practice of pharmacy in any of its branches. The retail pharmacist often makes chemical and microscopical examinations of urine, or even maintains a general commercial laboratory; and the chemist in a manufacturing house may be called upon to examine flue gases, coal, paints and other materials used in construction work, but none of these can be included in the branch of chemistry under consideration.

There are four well defined divisions of pharmacy in which chemistry plays an important part—Retail Drug Business, Pharmaceutical Education, Pharmaceutical Manufacturing, and Drug Inspection. These divisions originated in the order named and each is directly dependent upon those preceding it.

The retail drug store is the unit upon which the whole structure of pharmacy rests and from which the other divisions were evolved. A considerable knowledge of chemistry is required by the successful prescriptionist to whom many difficult problems come. The retail pharmacist also manufactures a certain number of his preparations, and his manufacturing operations should differ only in magnitude from those of the manufacturing pharmacist which we shall consider later. The retail pharmacist should also be competent to inspect his purchases of drugs and chemicals and this requires careful analytical work. Hence, the purchase of a medicine at the drug store or the compounding of a prescription should not be considered as a commercial transaction, but as a professional service and should be paid for accordingly. While conditions in pharmacy are not ideal, rapid advancement is being made and the attitude of the public toward the pharmacist, influencing as it does the financial returns of the business, will be an important factor in pharmaceutical progress.

In the early days of scientific pharmacy the education of the apprentice was an important duty of the proprietor, but as pharmacy developed, schools were organized for the purpose of training men to act as retail pharmacists. Further progress, however, brought a demand for men trained to fill positions as chemists for manufacturing houses, boards of pharmacy, drug commissioners, etc. The schools have not met this demand and in most cases men must be selected who have a pharmaceutical education with very little chemical training or a good training in chemistry and no knowledge at all of pharmacy. The knowledge of chemistry or pharmacy which is lacking must then be obtained and, as the latter is more easily acquired, such positions are usually filled by men who have little or no knowledge of pharmacy. This condition is very unsatisfactory as the chemist may be handicapped for years by his ignorance of pharmaceutical conditions and facts which have never happened to come to his attention. It is true that attempts have been made by some of the colleges, to provide courses for chemists who wish to take up pharmaceutical work, but most of them have failed to provide training of the proper sort. Four-year pharmacy courses are often built up by taking a two-year course as a basis and attaching here and there a more or less unrelated subject until the time is reasonably well filled. Another idea is to devote a third year, after the regular two-year pharmacy course, to *food* and drug analysis. Bacteriology, botany, mineralogy, toxicology, urine analysis, water analysis, fire assaying and other interesting subjects are available for the construction of such courses; and there seems to be little realization of the fact that four years is a very short time in which to train men for pharmaceutical work, even if the curriculum is well chosen. The ideal training would include a knowledge of the retail drug business although this is not absolutely essential; the essential features are instruction in pharmacy and as broad a training in chemistry as possible. Of course, it is understood that mathematics, physics, languages and other subjects must be included in a course of this kind. Graduate courses of study should be established so that pharmaceutical chemists could pursue their studies under competent instructors.

We believe that the cause of this unsatisfactory condition in pharmaceutical education is found in the fact, already noted, that the men in any one of the divisions of pharmaceutical work have not sufficiently interested themselves in the work of the other divisions; and thus the educational men have had little opportunity to learn what is required in the other lines of work.

The chemical work of the manufacturing pharmacist is varied in character; and in order to gain a clearer idea of its nature it may be well to consider it in several steps. The inspection of crude materials is obviously a most important factor in the production of a good product. This inspection consists in the positive identification of everything purchased, exclusive of those things which are identified by a botanical examination; and as thorough a study as possible of the purity and strength of the material. Drugs of vegetable or animal origin containing known active principles must be assayed in order to deter-

mine their value. The determination of the nature and amount of impurities in organic and inorganic chemicals, oils, resins, gums, balsams, etc., taxes the resources of any chemist, and the pharmaceutical chemist is often driven to the expedient of rejecting clearly unsatisfactory materials on account of the presence of unidentified impurities. In choosing materials it is understood that certain amounts of harmless impurities must be permitted in all medicinal substances otherwise their cost would be prohibitive.

Having determined that the crude materials are satisfactory, the manufacturing processes must be controlled by the examination of preparations in different stages of manufacture in order to give directions for finishing products of proper strength and composition.

The finished products must then be examined to determine their compliance with standards of strength and purity, and also by aging experiments to determine something of their keeping qualities.

It is said that it is impossible to remain stationary; if this is true no manufacturer can stop when he has accomplished what has been outlined above; he must strive to advance. Many of the analytical methods used in this work leave much to be desired and a constant effort must be made to improve them. Manufacturing processes must be improved in order to produce better products and, to make them more economically, new processes and new products must also be devised.

With the enactment of food and drug laws the inspection of drug products became a very important division of pharmaceutical work. Extremely valuable results have already been achieved by workers in this field and by conservative work much more will be accomplished. The sensational methods and arbitrary rulings which have, in a few instances, been resorted to, are, however, to be greatly deplored.

Having discussed our subject in a general way it may be of interest to give some definite idea of the number of substances with which the pharmaceutical chemist has to deal. A certain manufacturing house lists about four thousand products, in the preparation of which about seven hundred different materials, which must be examined chemically, are used.

Pharmaceutical chemistry presents an inviting field of work to the young chemist. Comparatively little is known concerning the composition of many of the hundreds of vegetable drugs in use. Even in case of some of the most important drugs our knowledge is very defective. Ergot may be cited as an example, the most important contributions to our knowledge of its composition having been made within the last few years, although its study has been undertaken by many eminent chemists during a period extending over many years. The composition of the vegetable drugs alone offers an interesting and important field of work for the pharmaceutical chemist for generations to come. The effect of cultivation upon the chemical composition of medicinal plants has been almost entirely neglected, although the remarkable increase in the quinine content of cinchona bark through cultivation has long been known. The relation of chemical constitution to physiological action, and the study of the enzymes and hormones which may be used medicinally are merely suggestive of the broad fields which await the pharmaceutical chemist of the future.

While a review of the progress of pharmacy would not be appropriate here it may not be out of place to call attention to the several lines of coöperative analytical work which are being carried on. The keeping quality of medicinal preparations has already been referred to and this subject has had the serious consideration of manufacturers for a number of years. Several of the largest manufacturers have collaborated on this work and have published the results already obtained in the form of a brochure on the "Stability of the Drug Extracts." The work has shown that preparations of this class are as a rule remarkably stable.

The pharmaceutical division of this society has a Committee on Quantitative Methods whose function is the study and improvement of analytical methods used in pharmaceutical work.

The U. S. Pharmacopoeia and the National Formulary, which are our official standards for medicinal substances, are now being revised, and in these great undertakings a large number of workers in all branches of pharmacy are collaborating. As these works do not include all articles which are commonly used in medicine, the American Pharmaceutical Association has a standing committee for the establishment of unofficial standards in which all classes of pharmaceutical workers are represented.

As the pharmaceutical chemists are thus striving to advance this branch of chemistry, it is to be hoped that they will not neglect any opportunity for furthering closer relations with one another and with chemists in other lines of work.

F. R. Eldred.

ORIGINAL PAPERS

STRUCTURE OF GALVANIZED IRON.

By Walter Arthur and William H. Walker

Received December 11, 1911.

Galvanized iron, by which term in this article we shall include all zinc protected iron, consists not of a sheet of iron covered with a layer or skin of pure zinc, as one might expect, but, on the contrary, of a complicated system of iron-zinc compounds, starting with pure zinc on the outside and passing through these alloys to the iron base within. We shall consider the structure of zinc protected iron under the three heads:

1. Hot galvanized—material made by passing the iron through a bath of melted zinc.

2 Sherardized—the article heated in the presence of finely divided zinc and zinc oxide.

3 Wet or Electrogalvanized—a layer of either zinc or a zinc alloy deposited electrolytically on the iron article from an aqueous bath.

By examining the zinc-iron alloy diagram constructed by v. Vegesack,[1] which is reproduced in part as Fig. 1, we see that by raising the temperature iron

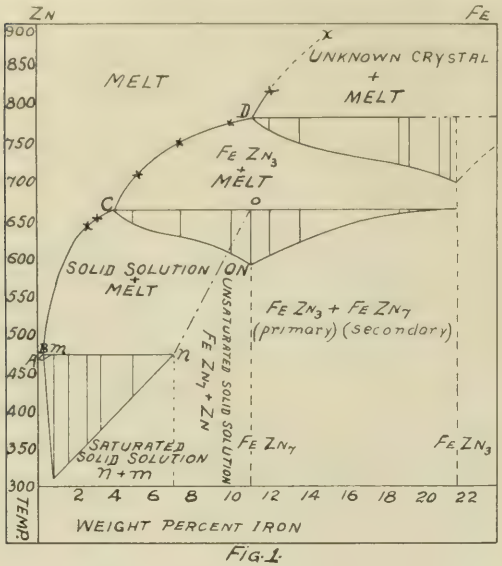

FIG. 1.

will dissolve in melted zinc to at least 24 per cent. Beyond this point it is impossible to go, owing to the volatility of the zinc. Hence the composition of the crystals separating along the dotted line DX is not accurately known, and will, for want of a better name,

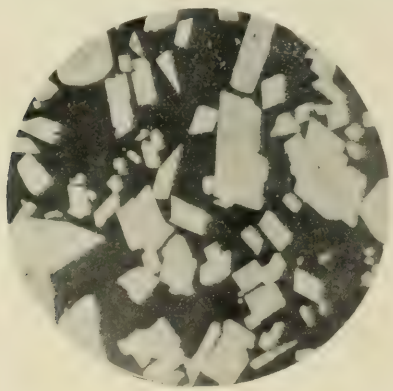

PLATE 1.

be called "binding alloy." From the molten mass at this point, crystals of this "binding alloy," $FeZn_3$, $FeZn_7$ (or a more or less saturated solution of zinc in $FeZn_7$), separate on cooling, the nature of the primary alloy depending on the concentration. The

[1] v. Vegesack, *Zeit. anorg. Chem.*, **52**, 30 (1907).

point n on the diagram represents the maximum solubility of zinc $FeZn_7$, and it is probably this saturated solid solution which is noticeable in certain sections of galvanized iron. A fraction of one per cent. (0.5–0.7 per cent.) of iron remains dissolved in the zinc after solidification.

Hot Galvanizing.—Consider first the ordinary method of galvanizing with reference to the equilibria indi-

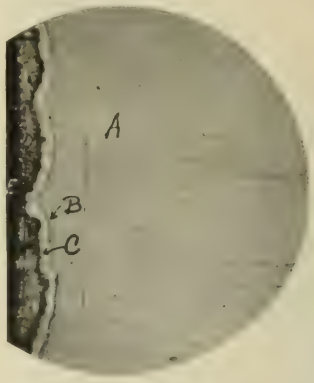

PLATE 2.

cated above. A piece of iron dipped into melted zinc at once begins to dissolve, the amount of solution depending on the length of time the iron is in the bath. As the solubility of iron in zinc is very low at this temperature the zinc bath soon becomes saturated, and a separation of the solid solution represented by the point n occurs. This crystalline compound is the "hard dross" of the galvanizer's bath and is shown in the photograph, Plate 1. There is also a tendency for equilibrium to establish itself on the surface of the iron, and as at this point of contact between molten zinc and solid iron all possible concen-

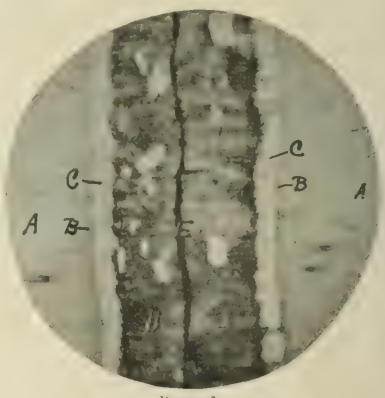

PLATE 3

tration may be considered to exist, the specific properties of the individual crystals determine the character and amount of each constituent. The actual behavior under varying conditions is best shown by microphotographs of the galvanized plates viewed in cross sections.

The preparation and polishing of plates in cross

sections presented some difficulties, the chief of which lies in the tendency of the zinc to "flow" in polishing,

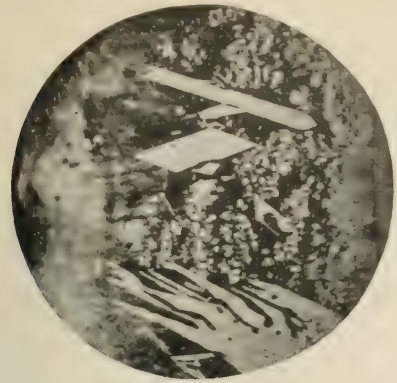

PLATE 4.

and the ease with which it gives rounded or "burred" edges when cut at right angles. To prevent "burring" several strips of the iron were immersed in sodium

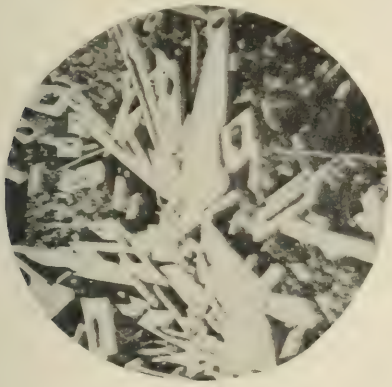

PLATE 5.

silicate solution until the surfaces were thoroughly covered, clamped tightly together in a small hand vise and dried for about two hours at 100° C. The

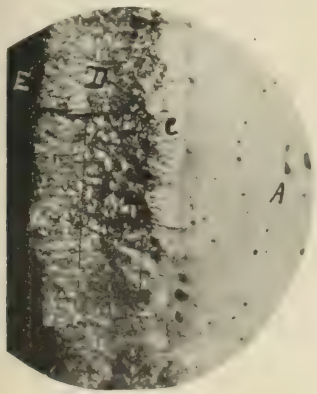

PLATE 6

hardened sodium silicate served to fill out the interstices resulting from the unevenness of the galvanized iron surfaces, thus preventing the burring of the edges at such points and the filling of such spaces by zinc

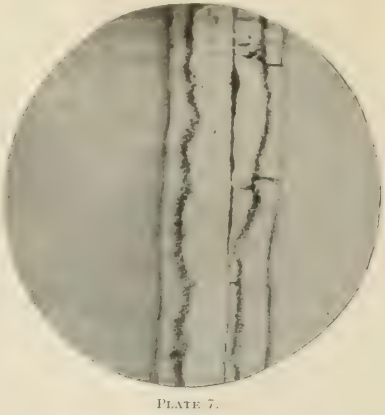

PLATE 7.

and iron particles in cutting and polishing. After the sodium silicate had thoroughly hardened, the edges of the pieces were all cut to the same plane by means

PLATE 8.

of a fine file, the final strokes being made in alternate directions so as to prevent any flowing of the zinc. The file was followed by fine emery paper, and this by

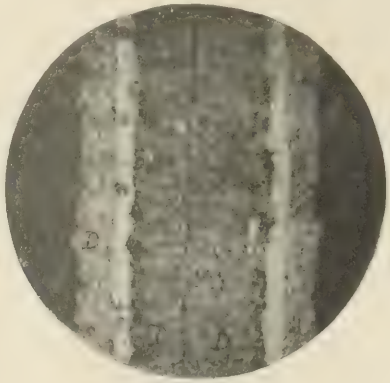

PLATE 9

still finer emery paper until the edges presented an unscratched surface to the unaided eye. The final

polishing was done on soft cotton flannel, mounted on a piece of rubber, and covered with jeweler's rouge.

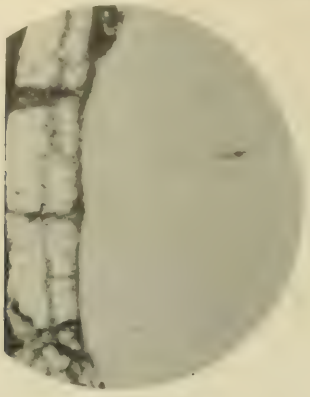

PLATE 10

In order to secure the best results, the final strokes were made very slowly and with a light pressure and always in alternate directions: 0.5 per cent.

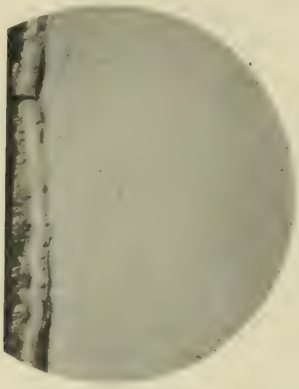

PLATE 11

nitric acid in 95 per cent. alcohol was used as an etching reagent. By means of a micrometer eye piece the thickness of the various layers found in the etched

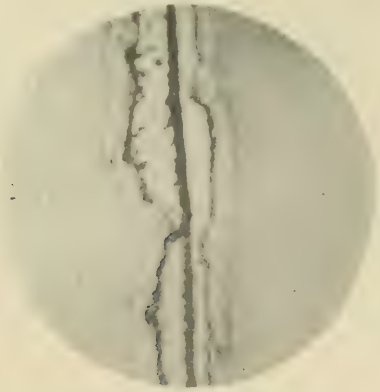

PLATE 12

specimens was measured. Each division of the scale shown in certain of the photographs represents 0.072 mm. on the specimen. Plate 2 shows a section of ordinary hot galvanized iron in which A is the iron, B

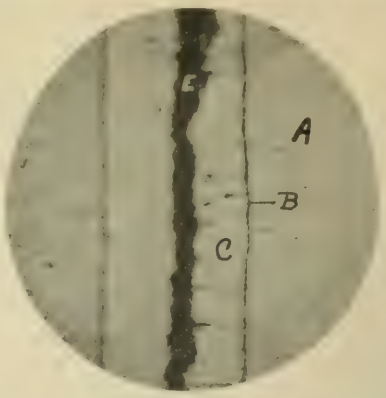

PLATE 13

a very thin layer of the "binding alloy" of undetermined composition, C the compound $FeZn_3$, D the zinc layer which is filled with tiny crystals of $FeZn_7$,

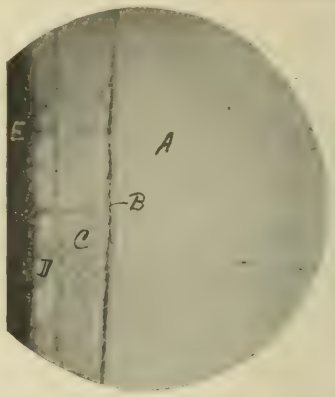

PLATE 14.

not visible in the photograph, and finally the sodium silicate. Plate 3 shows a section of heavily galvanized iron in which, because of a longer period of

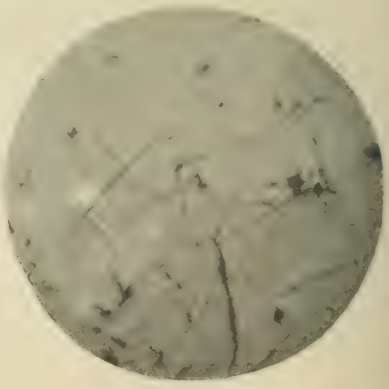

PLATE 15.

immersion in the zinc bath, much larger crystals of $FeZn_7$ have formed. The large increase in the amount

of the compound $FeZn_7$ due to abnormally long immersion in the zinc bath is shown in Plates 4 and 5.

That the tiny crystals of $FeZn_7$ are always present in the outer zinc layer can be determined in another way. If an ordinary galvanized plate is cautiously treated with caustic soda it is possible to dissolve the zinc without affecting the compound. On a surface

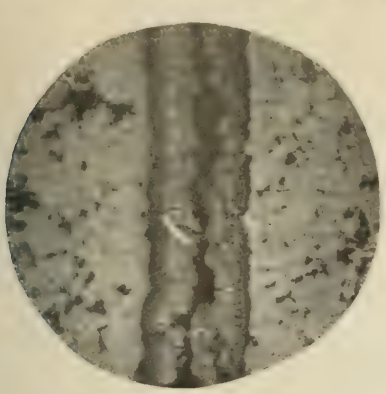

PLATE 16.

prepared in this way the tiny needle-like crystals of the compound become visible against the darker polygons of zinc.

Plate 6 is a cross section of a piece of galvanized pipe used and left by the French at Panama. It is remarkable that after an exposure of some thirty years there should still remain so unusual a coating of zinc. The layer of alloy $FeZn_3$ is also very heavy and the zinc is full of small crystals of $FeZn_7$, both facts indicating that the pipe was immersed for a considerable length of time in the galvanizing bath, and that the bath was fully saturated with $FeZn_7$.

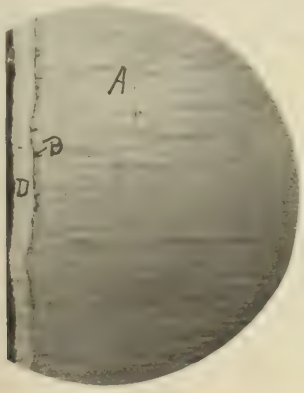

PLATE 17.

Plate 7 is two pieces of ordinary galvanized iron, one very irregular in thickness, which have been so etched as to bring out more strongly the binding alloy B.

We have already corrected[1] a statement erroneously made by one of us[2] that these alloys were electronegative to iron. While not so electropositive as zinc, they are *not* electronegative, and hence afford a distinct protection to the iron base. Plate 8 represents two parts of a galvanized sheet which had been exposed to the weather for a number of years. The left side is from a spot which showed no corrosion, and exhibits a continuous layer of zinc on the alloy $FeZn_3$. The right side was selected from a spot very close to where corrosion of the iron had already commenced. Only the alloy is left and this is broken through at one or two points. Plate 9 shows two sections of heavily galvanized iron which had been allowed to rust in a damp place, but which have not been artificially etched. A is the rusted iron surface. B is a strip of iron surface next to the alloy which has been protected from corrosion by the electropositive character of the alloy. C is the alloy and D the zinc.

A property of galvanized iron with which all users are familiar is its tendency to crack and peal off when

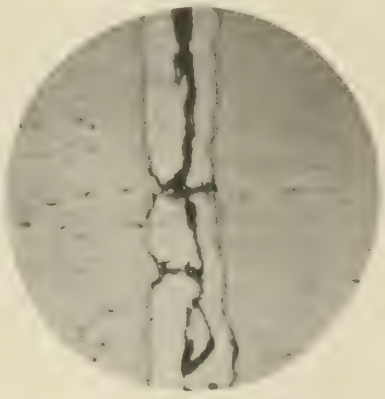

PLATE 18.

sharply bent. Investigation of cross sections made of specimens which had been bent showed that the parting of the galvanized coating from the iron takes place at the surface of the "binding alloy." This is as would be expected, inasmuch as the high iron alloys are very brittle. Such a break is shown in Plates 10 and 11.

Another property of galvanized iron is that of blistering with subsequent "flaking off" when heated, such, for example, as is seen on the flue of a house furnace. It was at first thought that the phenomenon was due to oxidation, but experiments carried on in an atmosphere of hydrogen and also carbon monoxide showed that this flaking occurred when the galvanized article reached a temperature of 360° C., or thereabouts. A polished section shows that in this case the parting takes place between the zinc and the alloy $FeZn_3$. Plate 12 shows such a structure. The black space between the alloy and the zinc is sodium silicate which has flowed in between the two layers.

Sherardized Iron.—The material known as sherardized iron is not a definite structure, but differs

[1] Patrick and Walker THIS JOURNAL, 3, No. 4 1911.
[2] Walker, *Proc. Am. Electrochem. Soc.*

according to the temperature, time and composition of the zinc powder mass employed. When the zinc powder is diluted with inert material, such as silica, and the time relatively short, the coating will consist of a very thin layer of the alloy $FeZn_8$, together with a more or less distinct layer of binding alloy of unknown composition. If the time is increased, and the powder richer in metallic zinc, a heavy coating is obtained as shown in Plate 13. If continued long enough, a layer of zinc forms on the surface of the alloy as shown in Plate 14. In all sherardized coatings are to be seen many cracks running through the alloy. This is particularly shown in the upper part of Plate 13. By polishing a section at right angles to the cross section, Plate 15 is produced. This shows the alloy to be broken into numberless fissures much resembling mud cracks. It is probable that greater study of etching methods would bring out still other alloys in this complicated structure. Thus Plate 16 shows two sherardized sections which have been etched by slow rusting in the air. They are from the same sheet as that used in Plate 13, and show a second alloy between the main coating alloy and what we have called the binding alloy. The blotched portions are the iron surfaces spotted with rust flecks. Owing to the brittleness of the main alloy a regular outline at the sodium silicate surface is difficult to obtain.

Electrogalvanized Iron.—The metal deposited by an electric current depends upon the impressed voltage and the composition of the electrolyte or bath. A coating of very pure zinc may be produced, or an alloy of widely varying proportions of iron may be obtained by adding iron salts to the bath, or as is sometimes erroneously done, by using an iron anode. In any case a very thin binding alloy next to the iron is always to be seen. Plate 17 shows a piece of ordinary wet galvanized iron in which the coating D is pure zinc. E is the sodium silicate layer, and B the binding alloy. Plate 18 shows two pieces of such iron which have been bent before mounting. The coating is seen to have parted from the iron base along the line formed by it and the alloy.

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THE ESTIMATION OF OXYGEN AND OCCLUDED GASES IN COPPER AND A CORRECTION TO THE ELECTROLYTIC ASSAY IN THE COMPLETE ANALYSIS OF COPPER.

BY GEORGE L. HEATH.

Received January 2, 1912.

The only strictly quantitative chemical reaction for the estimation of the oxygen in commercial copper was first proposed by Dr. W. Hampe,[1] of Germany. He subjected the finely divided metal to a gentle heat for a few minutes in a current of pure carbon dioxide, called the loss (a few mg.) moisture and ignored it: the oxygen was then determined by the loss of weight, or water produced, on heating in a current of hydrogen at red heat. His method was improved[2] by simplifying the cleaning of the metal and by absorbing the traces of evolved sulphur in an ammoniacal solution of cadmium chloride.

To secure the complete evolution of all gases from the metal, it is necessary to take a precaution not mentioned in any published description of the method. It is the purpose of this paper to correct the serious error in the old method[3] and to report the result of a search for a means of estimating the occluded gases in cast refined copper.

The loss on heating copper filings, or fine drillings, in hydrogen, until there is no further change in weight, is not entirely[2] due to oxygen from cuprous oxide and sulphurous acid, but also includes the gases derived by the metal from the fuel and the refining in the furnace, and in addition, any trace of moisture, mechanically held, and finally is subject to the error to be explained.

I have found that, within the limits of an ordinary analysis, red-hot copper has practically no affinity for carbon dioxide. It has been proved that the gases which exist in cast metal (0.005 per cent. or more) can be driven out of the same by replacing every trace of air in the glass tube with perfectly pure, dry carbon dioxide, and then heating the copper in contact with the gas for 20–30 minutes. The loss in weight is due to evolution of the occluded H, with traces of CO, CO_2, N, and possibly argon.

The loss of weight found by heating subsequently in hydrogen *does not express the true oxygen* of the cuprous oxide present in the cast metal, for the metal retains, after long exposure to a current of hydrogen, nearly twice as much hydrogen in an occluded state, or solid solution, as was present in the absorbed gas of the cast metal; the original occluded hydrogen gas was driven out by the preliminary heating in carbon dioxide. This serious error has hitherto escaped attention. The hydrogen held back after heating in hydrogen should be finally expelled from the reduced copper by a current of pure carbon dioxide, exposing the hot metal to this gas for twenty minutes before cooling and weighing in air.

Carbon Dioxide.—Carbonic acid free from every trace of oxygen and other impurities cannot be produced as easily from marble, or calcite, as by the method of Bradley and Hale.[3] They use a paste of sodium bicarbonate and water in a 700 cc. flask surmounted with a separator tube. The generator is started half an hour before use and the gas allowed to flow through the purifying and drying tubes (to be described), as far as a three-way valve placed just before the ignition bulb tube containing the copper. If the gas is generated from marble, or calcite, it is even more necessary to absorb the trace of oxygen constantly given off from the mineral after the air is all driven out of the apparatus. If a trace remains it will tint the red-hot metal at the point where it enters the bulb.

[1] *Z. f. Berg Hütten- and Salinen Wesen*, **1873**. Fresenius *Zeit.*, **1874**.
[2] Archbutt: *Analyst*, **25**, 253. Hoffmann: *Trans. A. I. M. E.*, **34**, 671. Heath: *Jour. Am. Chem. Soc.*, **27**, 313.
[1] Described by the author in *Jour. Am. Chem. Soc.*, **27**, 313.
[2] *J. Elect. Chem.*, **16**, 707. *Chem. Abstracts*, **1911**, p. 3384.
[3] *J. Am. Chem. Soc.*, **30**, 1090 (1908.)

The carbon dioxide is purified and dried as follows: (A) Casamajor generator with elevated pressure bottle, and small bottle on the table, containing the marble on a bed of large lead shot; the upper bottle is filled with hydrochloric acid (1 part to 2 of water). (A_1) Bulb of saturated, neutral $KMnO_4$. (B) Glass-stoppered U-tube sealed at the bottom with a solution of silver sulphate. (C) Bowen's (potash) bulb filled with strong sulphuric acid, after which may be placed a short tube of anhydrous calcium chloride. (D) A tube of dry chromous chloride.[1] (E) Tube of stick-phosphorus. (F) Two tubes of phosphorus pentoxide. (G) Short tube of dry calcium chloride. The expensive chromous chloride can be regenerated by passing a current of pure hydrogen through the tube at a gentle heat as long as any hydrochloric acid or moisture is given off.

By pulling out the second stopper in the tube B, the gas may be allowed to discharge into the air until the air is swept out of the generator, or it may be discharged under pressure from under a seal of 30 mm. of mercury, if generated from sodium bicarbonate by the method of Bradley and Hale.[2] The gas should always be passed through the bulbs as far as a three-way valve placed in front of the ignition tube until a test on hot copper shows that the gas is pure, giving no discoloration whatever at the point nearest the generator.

Hydrogen Gas.—The part of the generator holding the pure granulated zinc should be rather small, in order that the air may more easily be swept out. The action should be started and the gas passed over the copper for 15 minutes before lighting the burners. The purifying train[3] is as follows: A small washing bottle of 10 per cent. KOH, saturated with $KMnO_4$. Bowen's bulb, conc. sulphuric acid, (C) palladium asbestos tube, heated by alcohol lamp, after air is expelled. (D) An Allihn 250 cc. washing bottle containing 100 cc. of water, 100 grams of KOH (alcohol free) and 5 to 10 grams of pyrogallic acid. (E) Two tubes of dry calcium chloride and the three-way valve in succession (C and D, alternative, tube of stick P, and two tubes of phosphorus pentoxide).

Preparation of the Copper Sample for Ignition.—If a lot of copper is very porous, or of unknown origin, it may be advisable to dry it at 100° C. in an atmosphere of pure carbon dioxide or nitrogen (instead of heating in ignition tube to a heat which would expel some of the gases—an operation recommended by Hampe originally). If the speed and size of drill are regulated to produce fine drillings without any heating and oxidation, or contamination from grease, it will not be necessary to clean the drillings with ether. The adoption of the Copper Specifications of the American Society for Testing Materials will secure a fair sample of any casting, although equally good results are assured by boring half way through from both top and bottom, and also from the sides. With very pure material, an inch in depth is sufficient, the oxide having been previously removed by starting the hole through the surface skin with a larger drill.

As a prominent chemist has just noted: "It is impossible to remove all the soapy lubricant, or organic matter, from wires by washing with alcohol or ether directly." In such cases, it is suggested that the wire be cut in three-inch pieces and digested for a few minutes with alcohol KOH, 1 per cent. strength, as warm as possible without producing oxidation, then wash in water, alcohol, and ether successively. If a slight abrasion of the "skin" is not objectionable, the wire could be scoured, wet, with sharp silica (ground to pass a 40-mesh sieve), then washed with alcohol, etc. Extraction with petroleum ether (88° to 85° Bé.) in a Soxhlet tube will sometimes remove the offending material.

The ignition is performed in a hard-glass tube about 30 cm. long and 6 mm. internal diameter, which has one long bulb, or two round ones, at the center. It is cleaned, ignited, weighed, and the 50 gram sample fed into the tube very quickly in the following manner: Slide a tight fitting rod into one end as far as the nearest bulb, and attach to the other end, by short tubing, a short-stemmed funnel, whose diameter equals that of the tube. By using a long platinum wire, and tapping the tube, the drilling can be packed in the bulbs, after which the tube is wiped with a dry warm cloth and allowed to stand 10 minutes on the balance before weighing. When connected with the apparatus, the ignition tube rests on a lamp ring of 10 cm. diameter, and is protected from overheating by wrapping it with a fresh piece of thin asbestos paper, held in place by a short piece of stiff bent platinum wire.

IGNITION OF COPPER.

For Absorbed Gases.—A short drying tube and jet tube can be attached to the rear end of the ignition tube through a glass three-way valve and the carbon dioxide passed through the tube system for 30 minutes to sweep all the air out of generator and tubes. The fan burner, or triple Bunsen burner, is then lighted, the copper kept at a full red heat for 20 minutes, the tube cooled with an air blast and the CO_2 replaced by air which will require 10 minutes. The tube is then wiped clean and allowed to stand on the scales 10 minutes before weighing. The loss is due to gases from the cast metal.

For Total Oxygen and Sulphur.—Pass in hydrogen for 15 minutes, then keep at a red heat (not high enough to distil the metal into the glass) for 1 hour if the sample is filings, or 2 hours for coarse drillings. The necessary time should be ascertained in each laboratory by repeating an ignition on drillings of their standard fineness, until the weight is constant. The three-way valve at the rear of the ignition tube should be turned during this heat so that the gases pass through a small U-tube, or bottle, containing 10 cc. of a solution of ammoniacal cadmium chloride (20 grams per liter). Start the current of CO_2 through its own set

[1] Recommended by J. O. Handy.

[2] *J. Am. Chem. Soc.*, **30**, 1090 (1908).

[3] Handy proposes the following alternative: (1) KOH, (2) conc. H_2SO_4, (3) $CaCl_2$, (4) heated palladium asbestos tube, (5) dry P_2O_5 opened up with glass wool.

of purifying tubes 20–30 minutes before the copper is all reduced, so that every trace of air shall be swept out of the tubes as far as the three-way valve in front of the copper. When the hydrogen has been passed long enough to complete the reduction of all oxides in the metal, turn off the hydrogen and pass in pure CO_2 for at least 20 minutes. Then cool the tube with an air blast until the copper is but slightly warm, replace the CO_2 with air and weigh with the same precautions as before.

Sulphur.—About 70 cc. of water are placed in a No. 1 beaker, the cadmium solution and sulphide washed into it with the aid of dilute hydrochloric acid (1 : 1) and the sulphur is titrated[1] at once with standard iodine (2 grams of I per liter). 1 cc. of this solution = 0.00025 gram of S.

Experimental proof of the completeness of the reduction of the copper by ignition in hydrogen and carbonic acid may be obtained by a careful electrolytic assay of the reduced drillings. The sum of the per cent. added to that of the other impurities as found by complete analysis will total 100 per cent. without any oxygen, if the work and sampling are correct. In order to attain such a result it will be found necessary to take the sample for oxygen determination from the very same bottle of drillings employed for the complete analysis, that is for the electrolytic assay of the original cast copper. In sampling a casting, the per cent. of oxygen varies directly with the per cent. of copper and silver and is variable enough in different samples drilled in the same casting to prevent the results adding up exactly 100 per cent on complete analysis unless one sample is used for all tests.

There is slightly less occluded gas in low-set, or oxidized, cast copper than in copper which is well refined to standard grade. Highly refined metal which shows "true" over-poling (due not to sulphur, but to poling too high in the furnace) would certainly show a large increase in occluded gases, near the upper surface of the castings of chilled metal.

Since the occluded gases in cast copper are so small in weight, a sample of 100 grams in a bulb of the style recommended by Dr. H. O. Hofmann would give a better result than the quantity I have specified.

CORRECTION TO ELECTROLYTIC ASSAY IN COMPLETE ANALYSIS OF COPPER.

The exact electrolytic assay of refined copper as described elsewhere by the author[2] gives results sufficiently accurate for valuation of the metal, but the deposition on the cathode is not absolutely complete when a test of 1 cc. of electrolyte with hydrogen sulphide remains colorless.

As noted by W. C. Ferguson in a recent paper, we have also observed that about 0.005 per cent. to 0.00 per cent. remains in solution.

When an accurate complete analysis of the metal is desired, the author is accustomed to treat the electrolytes from the 5- or 10-gram battery assays with hydrogen sulphide gas. The sulphides are collected on filter, roasted directly in a porcelain crucible, treated with a few drops of nitric and sulphuric acids, diluted with a little water, and the copper deposited on a small weighed platinum strip, and added to the principal cathode copper. Electrolytic deposits on platinum as obtained by strictly following the method just quoted, have been found to be free from any appreciable quantity of absorbed hydrogen.

The methods already described might be used for gases in steel,[2] by substituting nitrogen for carbon dioxide. Only of late has the effect of oxygen in steel received the attention it deserves.

	Sample No. 1. a. Per cent.	Sample No. 1. b. Per cent	No. 2. a. Per cent	No. 2. b. Per cent.	No. 3. "Low set" Per cent.	No. 4 Arsenical Per cent.
OCCLUDED GASES AND COMBINED OXYGEN IN REFINED COPPER						
Absorbed gases—by heating in CO_2	0.0064	0.0064	0.0074	0.0070	0.0070	0.0058	0.0077
Apparent loss—heating to constant weight in H gas and cooling in H gas			0.0523	0.0659	0.0579		0.0610
Additional loss by heating next in CO_2			0.0156	0.0132	0.0139		0.0018
Total Oxygen—by heating in H gas followed by CO_2 gas	0.0238	0.0254	0.0679	0.0741	0.0718	0.1664	0.0628
SUMMARY OF COMPLETE ANALYSIS.							
Oxygen and occluded gas averages		0.0310			0.0784	0.1722	0.0705
Foreign metals in copper		0.0081			0.0066	0.0080	0.0146
Arsenic							0.0674
Copper and silver		99.9560			99.9210	99.8120	99.8420
Total		99.9951			100.0060	99.9922	99.9945
PROOF OF METHOD FOR OXYGEN, ETC., BY ANALYSIS OF CU FROM IGNITION TUBE.							
Sulphur evolved and titrated		0.0006			0.0003		0.0011
Electrolysis (Cu and Ag)		99.9920			99.9930		99.9070
Foreign metals in Cu		0.0081			0.0066		0.0820
Total		100.0007			99.9998		99.9901

[1] We use a specially prepared starch indicator which gives a very clear blue, with none of that disagreeable muddy red, given by ordinary starch (*Am. Chem. Abstracts*, **4**, 2617). The starch is allowed to stand over night, covered with cold water, containing 0.001 per cent. of hydrochloric acid. The next morning the acid is carefully washed out and the starch dried for two hours in an air oven at 100° C. Five grams of this prepared material is boiled with 500 cc. of water, filtered, or decanted from the sludge, and 15 drops of oil of cassia added before bottling, to render the solution permanent: 3 cc. of starch indicator are used in each test; a deduction is made for the iodine required to produce the end point, as determined by a blank titration.

[1] THIS JOURNAL, **3**, Feb., 1911.

[2] *Ibid.*, **3**, June, 1911, p. 372.

SOME OBSERVATIONS ON THE DISINTEGRATION OF CINDER CONCRETE.

By George Borrowman.

Received Feb. 8, 1912.

Cinders, as an aggregate in concrete, are used rather commonly where a light, cheap mixture is desirable; also in fire-proof construction and perhaps in the latter capacity this kind of concrete finds its most important application.

Its efficiency, however, has been the subject of considerable discussion. Various tests have been made, the results of which tend to show the superiority of this material over all other fire-resisting substances. There are also several patented floors involving cinder concrete which have been used successfully. Nevertheless, it has failed in some instances when employed for ordinary purposes, cracking and disintegration taking place. These discordant results are due, no doubt, as Freitag suggests in his "Fire-proofing of Steel Buildings," to the use of cinders of varying quality, but to the writer's knowledge the matter has not been further investigated. A particular case of disintegration, accompanied by a powdery efflorescence on the surface of the concrete, was observed by Dr. S. Avery, now Chancellor, but formerly head of the department of chemistry in this University, who prompted some study of the phenomena and also made various helpful suggestions during the experiments.

Blocks of concrete containing cement, sand and quarter-inch cinders were first prepared, the proportions by weight being 1 : 2 : 3, respectively. The cinders were from steam coal and slack and were carefully screened. The cement and sand were of good quality, the latter being sieved through twenty-mesh onto thirty.

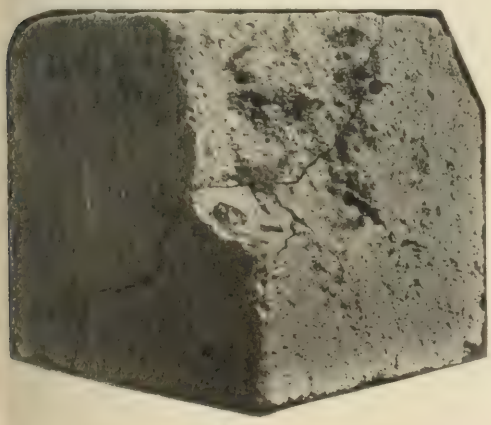

Fig. 1.

Another lot was then made up using cinders from one-half to one inch in size, the proportions being 1 : 1 : 1. In each case just enough water was used to insure thorough incorporation without running. All the blocks were placed on a glass plate to prevent loss of moisture and covered with a damp cloth for two weeks.

At the end of this period, the specimens having the proportions 1 : 2 : 3 showed no change but were somewhat porous and friable, owing to the relatively large bulk of cinders. A little later, however, fine cracks developed, with general disintegration. The others (1 : 1 : 1), though compact and hard, also

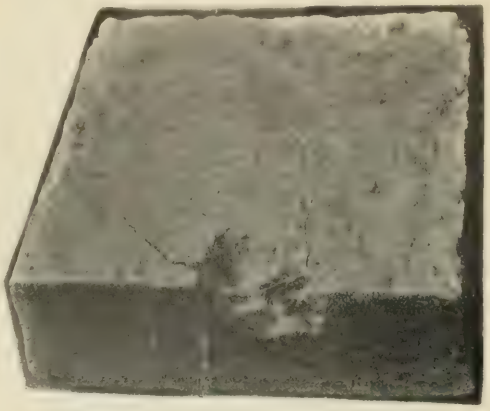

Fig. 2.

showed signs of cracking and in a short time the breaks became very pronounced. In each case they radiated from certain points.

These latter specimens were broken open to facilitate examination and in some cases the breaks originated from cinders that showed oxidation of much iron. The accompanying cuts show plainly these nodules and the mode of cracking. The surfaces of the concrete bounding the cracks crumbled easily, indicating more or less general weakening.

The appearance of these oxidized cinders suggested the presence, originally, of much ferrous iron, probably as sulphide. The analysis of the cinder stock showed considerable sulphur as sulphide and sulphate; also iron, though the proportion of ferrous iron could not be determined in material of this sort, with accuracy:

Analysis of Cinders.

	Per cent.
SiO_2	37.86
Total Fe as Fe_2O_3	21.16
Al_2O	17.40
CaO	10.96
MgO	0.85
S	0.60
SO_3	5.82
Undetermined (C, etc.)	5.37
	100.00

It seemed probable, then, from the foregoing data, that oxidation of iron and sulphur produced internal stress and consequent cracking, aided, no doubt, by the general weakness produced by the diffusion of soluble sulphates. This theory was further strengthened by finding that the efflorescence, found on the surface of the disintegrating concrete before mentioned, was ferrous sulphate.

On this assumption attempts were made to bring about similar results by substituting for cinders artificial iron sulphide, prepared in several ways.

These experiments, however, were not successful. On breaking open the blocks, the sulphide was found to be unchanged, surrounded by hard, compact cement. Soluble sulphates being absent in the mixture, the blocks had, of course, greater initial strength than those containing cinders and would have withstood considerable stress had there been any. The lack of

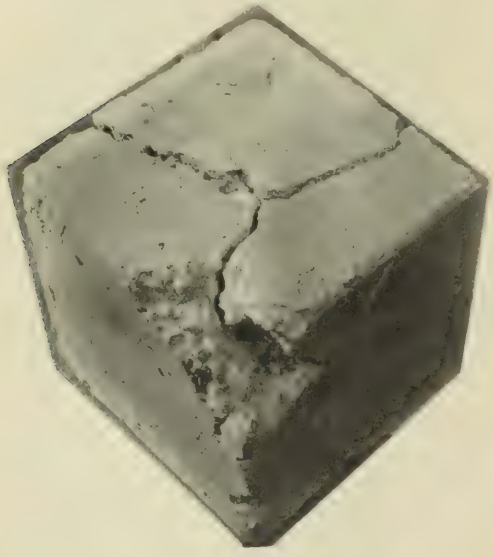

FIG. 3.

oxidation, though, in these tests, indicated that in the case of the cinders the necessary oxygen must have come from the cinders themselves, since they were equally well protected from the air.

This conclusion drew attention to the fact that about one-third of the cinder stock consisted of a very porous coke. As is well known, this substance will persistently occlude large amounts of oxygen. According to Starr and Lewis, air-dried coke contains absorbed gases in the proportion of about seven-tenths of a cubic centimeter per gram of coke, two to six per cent. of the gases being oxygen. The oxidation in the concrete was most pronounced in the coke. Moreover, some pieces of the latter were picked from the cinder stock and tested for sulphide sulphur, about one per cent. being found. The nodule from which the cracks radiate in Fig. 1 proved to be a piece of coke so thoroughly oxidized as to look like a mass of ferric oxide. This was tested and found to contain but a trace of sulphur.

As a final experiment, some of the original stock of cinders were kept exposed to air and moisture until, on washing, they showed the presence of no soluble sulphate. They were then made into a block of concrete similar to those prepared before (1 : 1 : 1). Under parallel conditions no disturbance took place, the material retaining perfect stability.

From these tests we may conclude that cinders with much sulphide and sulphate sulphur are likely to give unsatisfactory results, especially if there is much coke or porous material present; also that such material may be improved if allowed to weather, with occasional washing, until the ferrous iron and sulphur have been oxidized and leached out.

UNIVERSITY OF NEBRASKA,
LINCOLN.

SOME PROBLEMS IN CHEMICAL ENGINEERING PRACTICE.[1]

THE MANUFACTURE OF CHLOROFORM FROM BLEACHING POWDER AND ETHYL ALCOHOL.

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Received January 5, 1912.

(Concluded from the May No.)

Experiments Series F, comprising six experiments and representing six days' work in the plant, were made to determine whether that part of ethyl alcohol which is destroyed in the reaction can be substituted by methyl alcohol.

Apparatus Fig. 2 (page 350) was used, with 1500 cc. retort

The experiments were made in the same manner as the experiments of Series E, only the larger part of the ethyl alcohol was substituted by methyl alcohol.

1. Materials used: 100 grams bleach, 35 per cent.; enough water to make 500 cc.; 20 cc. ethyl alcohol, 94 per cent.; 500 cc. methyl alcohol, 90 per cent. free of acetone; mixed at 20° C. and distilled. Products obtained: 1.2 grams chloroform washed, s. g. 1.48; 700 cc. diluted mixed alcohols (distillate A)

2. Materials used: 100 grams bleach, 35 per cent.; enough water to make 300 cc.; 20 cc. ethyl alcohol, 94 per cent.; 700 cc. distillate A; mixed at 20° C. and distilled. Products obtained: 3.7 grams washed chloroform, s. g. 1.48; 700 cc. diluted mixed alcohols (distillate B).

3. Materials used: 100 grams bleach, 35 per cent.; enough water to make 300 cc.; 20 cc. ethyl alcohol, 94 per cent.; 700 cc. distillate B; mixed at 20° C. and distilled. Products obtained: 5.2 grams washed chloroform, s. g. 1.48; 700 cc. diluted mixed alcohols (distillate C.).

4. Materials used: 100 grams bleach, 35 per cent.; enough water to make 300 cc.; 20 cc. ethyl alcohol, 94 per cent.; 700 cc. distillate C mixed at 20° C. and distilled. Products obtained 7.2 grams chloroform washed, s. g. 1.48; 700 cc. diluted mixed alcohols (distillate D).

5. Materials used: 100 grams bleach, 35 per cent.; enough water to make 300 cc.; 20 cc. ethyl alcohol, 94 per cent.; 700 cc. distillate D; mixed at 20° C. and distilled. Products obtained: 7.6 grams chloroform washed, s. g. 1.48; 700 cc. diluted mixed alcohols (distillate E).

6. Materials used: 100 grams bleach, 35 per cent.; enough water to make 300 cc.; 20 cc. ethyl alcohol, 94 per cent.; 700 cc. distillate E; mixed at 20° C. and distilled. Products obtained: 7.8 grams chloroform washed, s. g. 1.48; 700 cc. diluted mixed alcohols (distillate F).

TABLE VII.—COMPARISON OF EXPERIMENTS SERIES D AND F.

Number of experiment.	Bleach, 35 per cent., used. Grams.	Chloroform washed, s. g. 1.48, obtained in Series D.	Series F.
1	100	1.2	1.2
2	100	3.6	3.7
3	100	5.4	5.2
4	100	7.5	7.2
5	100	6.7	7.6
6	100	9.0	7.8

Conclusions from Series F.—Comparing experiments Series D and F, it is proven that the presence of large amounts of methyl alcohol (free of acetone),

[1] Address read at the Annual Meeting of the American Institute of Chemical Engineers, in Washington, D. C., December, 1911.

in presence of a small amount of ethyl alcohol, does not increase the yield of chloroform from bleach.

Experiment Series G, comprising nine experiments, were made for the purpose of studying the decomposition of chloral hydrate with water and hydrated lime.

It is supposed that the decomposition runs by the following equation:

$$2CCl_3CH(OH)_2 + Ca(OH)_2 = 2HCCl_3 + (HCO_2)_2Ca + 2H_2O$$

The chloral hydrate crystals and hydrated lime used for the following experiments were free from hydrochloric acid. Apparatus Fig. 2 was used with a 1500 cc. retort. In each of the following experiments 30 grams chloral hydrate were used which theoretically would require 6.71 grams $Ca(OH)_2$ for decomposition and would make 21.6 grams of chloroform. Hydrated lime was taken in excess of theory. This was done because the reaction was studied as part of the chloroform formation occurring in the action of bleaching powder upon alcohol, in which case hydrated lime was always present in excess. To secure quick mixing the chloral hydrate was used in form of solution having 30 grams chloral hydrate to 100 cc. The distillation was carried out as in the former experiments.

1. Materials used: 15 grams $Ca(OH)_2$; 1000 cc. water; 30 grams chloral hydrate dissolved in 70 cc. water; mixed at 18° C. and distilled. Products obtained: 15 grams chloroform and 40 cc. water.

The 40 cc. water were separated from the chloroform and returned to the retort together with additional 15 grams hydrated lime, and the distillation was repeated but no additional chloroform was obtained. The contents of the retort were analyzed for chlorine by filling up to 1500 cc., filtering off 50 cc. solution, neutralizing these 50 cc. exactly with nitric acid and titrating with standard silver solution, using potassium chromate as indicator. As much chlorine was found as is contained in 1.86 grams of chloroform.

The 1450 cc. of material not used for this analysis was acidulated with nitric acid to dissolve all of the hydrated lime, and in an aliquot part of the solution chlorine was determined by the gravimetric method of precipitating with silver nitrate and weighing as silver chloride. The result was the same as the value found by titration.

In order to find out whether the proportion of hydrated lime would influence the yield of chloroform, the same experiment was repeated with the same quantities of materials and under the same conditions with the only exception that the quantity of hydrated lime was varied. In all instances the materials were mixed at ordinary temperature and slowly heated until 50 cc. had been distilled over. The chloroform was then separated from the water, the latter being returned to the retort. In a second distillation, in no case was any additional chloroform obtained. The results were as follows, *viz.*:

2. Materials used: 25 grams hydrated lime; 1000 cc. water; 30 grams chloral hydrate, dissolved in 70 cc. water; mixed at 18° C. and distilled. Product obtained: 15.1 grams chloroform.

The contents of the retort were analyzed for chlorine in the same manner as described in Series G1, and chlorine was found equivalent to 1.53 grams chloroform.

The experiments with these proportions and the same temperature were repeated a second and a third time, with the following results:

2a. 15.75 grams chloroform were obtained and nitrate of silver would precipitate from the neutralized contents of the retort an amount of chlorine equivalent to 1.80 grams chloroform.

2b. 15.7 grams chloroform were obtained and nitrate of silver would precipitate from the neutralized contents of the retort an amount of chlorine equivalent to 1.78 grams chloroform.

Average of Series G2, 2a, and 2b. 15.5 grams chloroform and chloride of calcium, equivalent to 1.7 grams chloroform, were obtained, out of a possible total of 21.6 grams. The difference of 4.4 grams of chloroform, or its equivalent, was decomposed into other organic chlorine compounds.

3. Materials used: 50 grams hydrated lime; 1000 cc. water; 30 grams chloral hydrate dissolved in 70 cc. water; mixed at 18° C. and distilled. Products obtained: 15.3 grams chloroform and silver nitrate would precipitate in the acidulated contents of the retort an amount of chlorine equivalent to 1.46 grams chloroform.

Conclusion from Series G1, 2a, 2b, and 3.—A large excess of hydrated lime has no influence upon the yield of chloroform from chloral hydrate. In using 15, 25, and 50 grams of lime, respectively, upon 30 grams of chloral hydrate, 15, 15.5 and 15.3 grams chloroform were obtained in the respective experiments, and chlorine in inorganic compounds equivalent to 1.86, 1.70 and 1.46 grams chloroform could be precipitated from the residual material in the retort by silver nitrate. The respective values of chloroform added would give 16.86, 17.2, and 16.76 grams accounted for, as against 21.6 grams required by theory. This would tend to prove that under the conditions of the experiments a large proportion of the chloral hydrate is decomposed into organic chlorine compounds, not chloroform, which would account for part of the loss in the manufacture of chloroform from bleach and alcohol.

This series of experiments was continued by varying the temperature at which the materials were mixed and reacted upon. All the following experiments were executed in the same manner as Nos. 1, 2 and 3, with the only exception of the temperatures observed. In each case, the first 50 cc. water distilling over with the chloroform were returned to the retort and upon repeated distillation no additional chloroform was obtained.

Apparatus Fig. 2 used with 1500 cc. retort (long stem funnel in retort).

4. Materials used: 25 grams hydrated lime; 1000 cc. water; heated to 80° C.; 30 grams chloral hydrate; 70 cc. water; 18° C. warm poured by a long stem funnel into the milk of lime contained in the retort and distilled. Products obtained: 16.5 grams chloroform and silver nitrate would precipitate from the neutralized contents of the retort an amount of chlorine equivalent to 1.52 grams of chloroform.

5. Materials used: 25 grams hydrate of lime; 1000 cc. water; heated to boiling point; 30 grams chloral hydrate; 70

cc water 18° C. warm poured by a long stem funnel into the boiling milk of lime contained in the retort and distilled. Products obtained 18.4 grams chloroform and silver nitrate would precipitate from the neutralized contents of the retort an amount of chlorine equivalent to 1.11 grams of chloroform.

52 Experiment No. 5 was repeated in exactly the same manner.

18.4 grams chloroform were obtained and silver nitrate would precipitate from the neutralized contents of the retort an amount of chlorine equivalent to 1.39 grams chloroform.

As an average of 5 and 5*a*, 18.4 grams chloroform and chloride of calcium equivalent to 1.25 grams chloroform were obtained, out of a possible 21.6 grams.

The difference of 1.95 grams of chloroform or its equivalent was decomposed into other organic chlorine compounds.

Conclusions from Series G2, 2a, 2b, 4, 5 and 5a.—The temperature at which the materials are brought together is of marked influence upon the yield of chloroform from chloral hydrate and hydrated lime. The yield is greatest if the materials are mixed at the boiling point of their solutions.

The yield was, in three experiments, 15.1, 15.75, and 15.7 grams out of a possible 21.6 grams of chloroform, if the ingredients were mixed at ordinary temperature.

The yield was in one experiment 16.5 grams, out of a possible 21.6 grams of chloroform, if the ingredients were mixed at 80° C.

The yield was in two experiments 18.4 and 18.4 grams, out of a possible 21.6 grams of chloroform, if the ingredients were mixed at the boiling point of their solutions.

The destruction of organic chlorine compounds by action of hydrated lime was equivalent to the complete destruction of chloroform ranging from 1.11 grams to 1.86 grams, out of a possible 21.6 grams.

In all instances, some organic chlorine compounds, not chloroform, were produced, the amounts of which ranged from an equivalent of 1.95 grams to 4.4 grams chloroform, out of a possible total of 21.6 grams.

More organic chlorine compounds, not chloroform, were formed if the solutions were mixed cold than if they were mixed hot.

More chloroform was destroyed if the solutions were mixed cold than if they were mixed hot.

Experiments Series H, comprising four experiments and representing four days' work in the plant, were made to ascertain the influence of calcium hydrate upon the formation of chloroform.

The experiments, Series E*a*, were repeated with the variation that 20 grams hydrated lime were added to the charge in the retort in each experiment.

The yield in washed chloroform, sp. gr. 1.48, in four consecutive experiments was 6.5, 8.6, 10.3, and 11.1 grams, respectively.

Experiments Series H*a*, comprising four experiments and representing four days' work in the plant, were made to ascertain the influence of calcium hydrate upon the formation of chloroform.

The experiments, Series E*a*, were repeated with the variation that the 15.5 per cent. of free calcium hydrate, which was present in the bleach, was neutralized by 10 per cent. hydrochloric acid before addition of the alcohol. Temperature in mixing 20° C.

The yield in washed chloroform, sp. gr. 1.48, in four consecutive experiments, was 6.8, 9.1, 9.8, and 10.5 grams, respectively.

Experiments Series H*b*, comprising four experiments and representing four days' work in the plant, were made to ascertain the influence of calcium hydrate upon the formation of chloroform.

The experiments, Series E*a*, were repeated, with the variation that the 15.5 per cent. of free calcium hydroxide, which was present in the bleach, was neutralized by 10 per cent. hydrochloric acid before addition of the alcohol. Temperature in mixing 20° C.

Subsequently, the temperature was slowly raised until the chloroform reaction was induced (about 80° C.), which could be observed by the mixture becoming milky from separated hydrated lime. The contents of the retort were then neutralized again by adding 10 per cent. hydrochloric acid. The amount of hydrochloric acid used for the second neutralization corresponded to 6.5 grams $Ca(OH)_2$ as an average of four experiments: 2.4 grams $Ca(OH)_2$ were used up for the decomposition of organic chlorine compounds.

Finally, the chloroform and alcohol were distilled off in the same manner as described in the experiments, Series E.

The yield in washed chloroform, sp. gr. 1.48, in four consecutive experiments, was 67, 8.8, 9.9 and 10.8 grams, respectively.

TABLE VIII.—COMPARING RESULTS OF EXPERIMENTS SERIES H, H*a*, H*b* WITH E*a*.

Operation. No.	Series E*a*. 100 grams bleach, 35 per cent.; 200 cc alcohol, 94 per cent.; water to make 100 cc. Temperature 20° C. made chloroform. Grams.	Series H. 100 grams bleach, 35 per cent.; 200 cc. alcohol, 94 per cent.; water to make 1000 cc.; 20 grams $Ca(OH)_2$. Temperature 20° C. made chloroform. Grams.	Series H*a*. 100 grams bleach, 35 per cent.; 300 cc. H_2O neutralized with HCl, 10 per cent.; 200 cc. alcohol, 94 per cent.; water to make 1000 cc. Temperature 20° C. made chloroform. Grams.	Series H*b*. 100 grams bleach, 35 per cent.; 300 cc. H_2O neutralized with HCl, 10 per cent.; 200 cc. alcohol, 94 per cent.; water to make 1000 cc. Temp. 20° C. heated and neutralized again with 10 per cent. HCl made chloroform. Grams.
1	6.75	6.5	6.8	6.7
2	8.4	8.6	9.1	8.8
3	10.5	10.3	9.8	9.7
4	110.9	11.1	10.5	10.8

Conclusions from Series Ea, H, Ha and Hb.—Larger or smaller quantities of hydrated lime present during the reaction have no marked influence upon the formation of chloroform from bleach and alcohol, but part of the calcium hydrate generated by the chloroform reaction combines *in statu nascendi* with chlorine coming from organic chlorine compounds. As an average from Series H*b*, 8.9 grams $(CaOH)_2$ were formed by the chloroform reaction, 2.4 grams of which combined again with chlorine taken from organic compounds, to make calcium chloride.

Experiments Series I, comprising three experiments and representing three days' work in the plant, were made for the purpose of determining the temperature at which the chloroform reaction takes place, and to ascertain the amount of

$Ca(OH)_2$ formed in the chloroform reaction. Apparatus Fig. 2 was used, with 2500 cc. retort.

A filtered solution of bleach in water, containing 35 grams of active chlorine and 2.3 grams $Ca(OH)_2$ in one liter, was used in the following experiments. One liter of this solution would correspond to 100 grams bleach, 35 per cent., containing 2.3 per cent. $Ca(OH)_2$, but no $CaCO_3$.

1. Materials used: 1000 cc. solution of bleach = 35 grams Cl; 200 cc. alcohol, 94 per cent.; mixed at 20° C. and distilled. Products obtained: 8.2 grams washed chloroform, s. g. 1.48; 700 cc. diluted alcohol (distillate A).

The chloroform reaction commenced at 60 to 65° C. and could easily be observed by the clear solution becoming milky, caused by separation of $Ca(OH)_2$.

The residue remaining in the retort after the distillation contained 8.14 grams $Ca(OH)_2$ by titration, a small part of which was combined with CO_2.

2. Materials used: 1000 cc. solution of bleach = 35 grams Cl; 700 cc. distillate A; mixed at 20° C. and distilled. Products obtained: 10.5 grams washed chloroform, s. g. 1.48; 700 cc. diluted alcohol (distillate B).

The chloroform reaction commenced at 60° to 62° C.

The residue remaining in the retort after distillation contained 7.96 grams $Ca(OH)_2$, some of which was combined with CO_2.

3. Materials used: 1000 cc. solution of bleach = 35 grams Cl; 700 cc. distillate B; mixed at 20° C. and distilled. Products obtained: 10.5 grams washed chloroform, s. g. 1.48; 700 cc. diluted alcohol (distillate C).

The chloroform reaction commenced at 60° to 65° C. and the residue remaining in the retort after distillation contained 7.95 grams $Ca(OH)_2$, combined with a small amount of CO_2.

Experiments Series J, comprising four experiments and representing four days' work in the plant, were made to ascertain the temperature at which the chloroform reaction takes place at various concentrations of alcohol.

The reaction could be observed by the clear solution becoming milky, caused by separation of $Ca(OH)_2$, and the completeness of the reaction could be measured by titrating the contents of the retort for $Ca(OH)_2$ with normal hydrochloric acid on the basis of the experiments in Series K.

Apparatus Fig. 2 used with 2500 cc. retort.

1. Materials used: 1000 cc. solution of bleach = 35 grams Cl and 2.3 grams $Ca(OH)_2$; 200 cc. alcohol, 94 per cent.; mixed at 20° C. and slowly heated. Products obtained: 8.2 grams washed chloroform.

The chloroform reaction commenced at 60° to 65° C. and was finished after boiling, the contents of the retort measuring 8.14 grams $Ca(OH)_2$.

2. Materials used: 1000 cc. solution of bleach = 35 grams Cl and 2.3 grams $Ca(OH)_2$; 1000 cc. alcohol, 94 per cent.; mixed at 20° C. it turned turbid very slowly. Titrated for $Ca(OH)_2$ after standing 24 hours at 20° C., it contained 6.97 grams $Ca(OH)_2$.

3. Materials used: 1000 cc. solution of bleach = 35 grams Cl and 2.3 grams $Ca(OH)_2$; 1200 cc. alcohol, 94 per cent.; mixed at 20° C.; reacted at once, without being heated, and after one hour the contents of the retort measured 6.99 grams $Ca(OH)_2$.

Conclusions from Series I and J.—The temperature at which the chloroform reaction takes place and the time which it requires depends upon the concentration of the alcohol in the charge.

Approximately 20 per cent. alcohol will react with bleach at 60° to 65° C.

Approximately 50 per cent. alcohol reacts with bleach at 20° C. within twenty-four hours.

Approximately 55 per cent. alcohol reacts with bleach at 20° C. instantly, without application of external heat.

Experiments Series K, comprising fourteen experiments and representing fourteen days' work in the plant, were made for the purpose of determining the amount of chloroform and $Ca(OH)_2$ formed by repeated reaction of 750 cc. of a filtered solution of chlorinated lime, containing 35 grams Cl and 1.7 grams $Ca(OH)_2$ on 200 cc. alcohol, 94 per cent.

No alcohol was added except in the first operation. Apparatus Fig. 2 was used with 2500 cc. retort.

The series is a repetition of Series E*a*, carried on to fourteen operations, the difference being that filtered solution of chlorinated lime was used instead of the solid salt, on account of which fact the $Ca(OH)_2$ which was formed by the chloroform reaction could be measured.

1. Materials used: 750 cc. solution bleach = 35 grams Cl, and 1.7 grams $Ca(OH)_2$; 200 cc. ethyl alcohol, 94 per cent.; 500 cc. water; mixed at 20° C. and distilled. Products obtained: 7.5 grams washed chloroform, s. g. 1.48; 700 cc. diluted alcohol (distllate A). The contents of the retort measured 7.4 grams $Ca(OH)_2$ by titration.

2. Materials used: 750 cc. solution bleach = 35 grams Cl and 1.7 grams $Ca(OH)_2$; 700 cc. distllate A; mixed at 20° C. and distilled. Products obtained: 8.2 grams washed chloroform, s. g. 1.48; 700 cc. diluted alcohol (distillate B). 7.1 grams $Ca(OH)_2$ in contents of retort.

This was repeated to fourteen operations and the results are entered in the following table:

TABLE IX.—EXPERIMENTS SERIES K.

Operations. No.	Chloroform washed. s. g. 1.48 obtained. Grams	$Ca(OH)_2$ in residue in retort. Grams.	$Ca(OH)_2$ in 750 cc. solution chlorinated lime. Grams.	$Ca(OH)_2$ formed by chloroform reactions. Grams.
1	7.5	7.4	1.7	5.7
2	8.2	7.1	1.7	5.4
3	9.0	7.5	1.7	5.8
4	9.8	7.9	1.7	6.2
5	10.2	7.2	1.7	5.5
6	9.4	7.7	1.7	6.0
7	9.8	7.2	1.7	5.5
8	8.6	7.3	1.7	5.6
9	8.2	6.6	1.7	4.9
10	8.6	7.2	1.7	5.5
11	8.2	7.5	1.7	5.8
12	6.7	6.6	1.7	4.9
13	8.0	7.5	1.7	5.8
14	6.0	7.7	1.7	6.0

Conclusion from Series K.—The amounts of chloroform and calcium hydrate formed in the chloroform reaction are in direct proportion.

Experiments Series L, comprising twenty-six experiments and representing twenty-six days' work in the plant.

The experiments of Series K were continued with the exception that determinations of lime were omitted after the fourteenth operation, to determine how much chloroform could be obtained from 200 cc. alcohol used in the first operation. The amounts of chloroform obtained in the subsequent operations are entered into the following table:

TABLE X. EXPERIMENTS SERIES L.

Series L No.	Bleach, 35 per cent., used 38 gr. Cl + 1.7 gr. $Ca(OH)_2$ in 750 cc. filtered solution. Grams.	Alcohol, 94 per cent., present. cc.	Chloroform, s. g. 1.48, obtained. Grams.	Alcohol, 94 per cent., used for chloroform reaction. cc.	Alcohol, 94 per cent., in after distillate. cc.
1	100	200.0	7.5	9.4	190.6
2	100	190.6	8.2	10.3	180.3
3	100	180.3	9.0	11.3	169.0
4	100	169.0	9.8	12.2	156.8
5	100	156.8	10.2	12.7	144.1
6	100	144.1	9.4	11.8	132.3
7	100	132.3	9.8	12.2	120.1
8	100	120.1	8.6	10.8	109.3
9	100	109.3	8.2	10.2	99.1
10	100	99.1	8.6	10.8	88.3
11	100	88.3	8.2	10.2	78.1
12	100	78.1	6.7	8.4	69.7
13	100	69.7	8.0	10.0	59.7
14	100	59.7	6.0	7.5	52.2
15	100	52.2	5.3	6.6	45.6
16	100	45.6	3.8	4.8	40.8
17	100	40.8	4.5	5.6	35.2
18	100	35.2	5.6	7.0	28.2
19	100	28.2	6.0	7.5	20.7
20	100	20.7	5.3	6.6	14.1
21	100	14.1	3.8	4.8	9.3
22	100	9.3	3.4	4.3	5.0
23	100	5.0	1.9	2.4	2.6
24	100	2.6	0.8	1.0	1.6
25	100	1.6	1.1	1.4	0.2
26	100	0.2	0.0	0.2	...
			159.7	200.0	

1.25 cc. alcohol, 94 per cent., made 1 gram chloroform.

Conclusion from Series L.—The amount of alcohol, 94 per cent., used for the chloroform reaction at a concentration of 10 per cent. or more is less than 1250 cc. of 94 per cent. alcohol to 1 kilogram of washed chloroform, or less than 15 gallons alcohol, 94 per cent., for 100 lbs. of chloroform.

Experiments Series M, comprising ten experiments, representing a run of ten days in the plant and designed for the purpose of determining the amount of alcohol, 94 per cent., used up in successive operations, the concentration of alcohol in the first operation being approximately 10 per cent.

Apparatus Fig. 2 was used, with 2500 cc. retort.

In each operation 750 cc. diluted alcohol were distilled which was used in the subsequent operation, together with 1.25 cc. alcohol, 94 per cent., and for every gram of washed chloroform obtained in the previous operation.

1. Materials used: 750 cc. solution bleach = 35 grams Cl; 150 cc. alcohol, 94 per cent.; 600 cc. of water; mixed at 20° C. and distilled. Products obtained: 7.8 grams washed chloroform, 1.48 s. g.; 750 cc. diluted alcohol (distillate A).

2. Materials used: 750 cc. solution bleach = 35 grams Cl; 10 cc. alcohol, 94 per cent.; 750 cc. distillate A; mixed at 20° C. and distilled. Products obtained: 9.0 grams washed chloroform, 1.48 s. g.; 750 cc. diluted alcohol, 94 per cent. (distillate B).

This was repeated to ten operations and the results are entered in Table XI.

The 750 cc. diluted alcohol coming from the tenth operation were diluted with an equal volume of water and redistilled with 20 grams hydrated lime, whereby 3.7 grams chloroform were obtained, together with diluted alcohol, containing 161 cc. alcohol, 94 per cent.

TABLE XI.

	Materials used.				Products	
	Bleach, 35 per cent., used in filtered solution.		Alcohol, 94 per cent., used.	Diluted alcohol from previous operation.	Chloroform, s. g. 1.48, obtained.	Diluted alcohol, distilled off after chloroform
Operation No.	Grams.	cc.	cc.	cc.	Grams.	cc.
1	100	1350	150	.	7.8	750
2	100	750	10	750	9.0	750
3	100	750	11	750	9.7	750
4	100	750	12	750	9.4	750
5	100	750	12	750	9.0	750
6	100	750	11	750	9.8	750
7	100	750	12	750	9.6	750
8	100	750	12	750	10.1	750
9	100	750	13	750	9.3	750
10	100	750	12	750	9.8	750
	1000	...	255	...	93.5	...

Conclusion.—1000 grams of bleach, 35 per cent., and 94 cc. of alcohol, 94 per cent., had, therefore, made 97.2 grams of washed chloroform, 1.48 sp. gr. The amount of alcohol, 94 per cent., used for the chloroform reaction, at a continuous concentration of 10 per cent., is approximately 968 cc. for 1000 grams washed chloroform, sp. gr. 1.48, or not quite 1 cc. alcohol, 94 per cent., for 1 gram of chloroform.

Experiments Series N, comprising ten experiments and representing a run of ten days in the plant. This series is a repetition of Series M, except that the materials were mixed near boiling point. (Compare Experiments Series G.)

Apparatus Fig. 1 was used, with 2500 cc. retort, carrying a long stem funnel, reaching toward the bottom of the retort.

The diluted alcohol was charged into the retort and heated to boiling, whereupon the solution of bleaching powder was poured, in small portions, through the long stem funnel into the alcohol, which was boiling in the retort.

The quantities of materials used were the same as in Series M, except the fresh alcohol, 94 per cent., was added at the rate of 1 cc. alcohol, 94 per cent., for every gram chloroform obtained in the previous operation. (See conclusion above.)

The results of ten operations are entered in the following table:

TABLE XII.

	Materials used.				Products.	
	Bleach, 35 per cent., used in filtered solution.		Alcohol, 94 per cent., used.	Diluted alcohol from previous operation.	Chloroform, s. g. 1.48, obtained.	Diluted alcohol distilled off after chloroform.
Operation No.	Grams.	cc.	cc.	cc.	Grams.	cc.
1	100	1350	150	...	7.2	750
2	100	750	7	750	9.8	750
3	100	750	10	750	10.4	750
4	100	750	10	750	10.8	750
5	100	750	11	750	10.9	750
6	100	750	11	750	10.2	750
7	100	750	10	750	11.0	750
8	100	750	11	750	10.8	750
9	100	750	11	750	11.0	750
10	100	750	11	750	10.6	750
	1000	. .	242	...	102.7	...

The 750 cc. of diluted alcohol coming from the tenth operation were treated in the same manner as described in Series M, whereby 3.2 cc. chloroform, sp. gr. 1.48, and 146 cc. alcohol, 94 per cent., were obtained.

Conclusion.—1000 grams bleach, 35 per cent., and 96 cc. alcohol, 94 per cent., had, therefore, made 105.9

grams of washed chloroform, sp. gr. 1.48, which would make 103.4 grams pure chloroform after washing with sulphuric acid 66° and redistilling. The amount of alcohol, 94 per cent., used for the chloroform reaction, at a continuous concentration of 10 per cent., is approximately 922 cc. alcohol, 94 per cent., for 1 kg. of washed chloroform, sp. gr. 1.48.

This work done, the most favorable conditions were figured from the conclusions Nos. 1 to 40, drawn from 126 experiments, which represent 126 days' work in the plant. They were found to be as follows, *viz.:*

1. The concentration of alcohol in the charge was to be about 10 per cent.

2. There was to be not less than 100 cc. alcohol, 94 per cent., present for every 100 grams of bleach, 35 per cent.

3. The alcohol and the solution of bleaching powder was to be brought together at boiling point, or as near to it as possible.

If these conditions could be given in the plant, 100 lbs. pure chloroform could be expected from 967 lbs. bleach, 35 per cent., and 11.5 gallons alcohol, 94 per cent. (see experiments Series N), in place of from 1510 lbs. bleach, 33$^1/_3$ per cent., and 11.73 gallons alcohol, 94 per cent., which were obtained as an average in the manufacture of 100,257 lbs. chloroform in actual practice (see Table I). While the consumption of alcohol was about the same as in the old process, the saving in bleaching powder was approximately 34 per cent.

In order to comply with these requirements one old apparatus, represented in Fig. 1 (p. 346), was changed as indicated in Fig. 3, by closing up the manhole in the still and riveting to the top of the still a funnel in the center of which a four-inch pipe reached down toward the bottom of the still. In place of a square box which, in the old process, had served for dissolving the bleaching powder, a round agitating apparatus, *A*, was installed, in which the bleaching powder was more readily dissolved in the necessary amount of water. The receiver *D*, taking the chloroform and diluted alcohol, which ran from the cooler, was changed to the form indicated in the drawing and a receiving tank, *E*, capable of holding 400 gallons of diluted alcohol, was set in the ground under the receiver, for the purpose of storing the diluted alcohol distilled in one operation. The bottom of the receiving tank was connected by a 1-in. pipe with the upper part of still *B*, and, by air pressure, the contents of the receiver could be blown out into the still as soon as the latter was ready for a new operation.

The apparatus was operated in the following manner:

120 gallons alcohol, 94 per cent., were charged into still *B*, Fig. 3, and sufficient water added to make the alcohol about 20 per cent. This would fill the still about 2 ft. One cask bleaching powder, holding about 1000 lbs., was charged into agitator *A*, containing sufficient water to fill the agitating vessel to within 6 inches from the top. Then the diluted alcohol was heated by direct steam to boiling, and the solution of bleaching powder was introduced into *B*, in small quantities, through the funnel tube.

The reaction would take place at once and the chloroform would distil freely, together with some alcohol. When all the bleaching powder was introduced, the chloroform, and subsequently the alcohol, were distilled off, about 400 gallons of diluted alcohol being obtained in each operation.

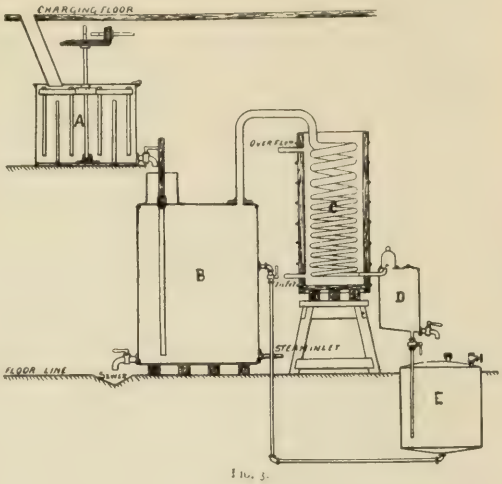


Fig. 3.

The diluted alcohol thus obtained was used for the subsequent charge and sufficient fresh alcohol, 94 per cent., was added to make up for the alcohol which had been converted into chloroform in the previous operation. With this alcohol and another 1000 lbs. bleaching powder, dissolved in sufficient water to fill the agitating tank *A* to within 6 inches from the top, the operation was repeated once a day and chloroform was thus obtained in a continuous run.

A run of six days was made with this improved apparatus, with the following results, *viz.:*

TABLE XIII.

Day.	Bleaching powder used. Bought for		Equal to		Alcohol, 94 per cent., used.	Chloroform, s. g. 1.48, obtained.	1000 lbs. bleach, 35 per cent., made chloroform, s. g. 1.48.
	Per cent.		Per cent.				
No.	Lbs.	Cl.	Lbs.	Cl.	U. S. gal.	Lbs.	Lbs.
1	1129	31	1000	35	120	81	81
2	1129	31	1000	35	10	100	100
3	1129	31	1000	35	10	102	102
4	1129	31	1000	35	10	108	108
5	1129	31	1000	35	10	106	106
6	1129	31	1000	35	10	105	105
Proportion.....			4000	35	...	421	105
			952	35	...	...	100

Not counting the first two days, in which the previous charges have an influence upon the yield, an average of 105 lbs. washed chloroform, sp. gr. 1.48, were obtained from 1000 lbs. bleach, 35 per cent.

An attempt was made to increase the capacity of the plant by charging 1500 lbs. of bleach, 35 per cent., into agitator *A* for each charge, adding sufficient water to make the same volume of solution as in the pre-

vious run, and using this more concentrated solution of bleach in the same manner as the weaker solution in the previous work.

TABLE XIV

Day	Bleaching powder used. Bought for		Equal to		Alcohol, 94 per cent., used	Chloroform, s. g. 1.48, obtained	1000 lbs. bleach, 35 per cent., made chloroform, s. g. 1.48
	Per cent.			Per cent.			
No.	Lbs.	Cl.	Lbs.	Cl.	U. S. gal.	Lbs.	Lbs.
1	1694	31	1500	35	120	125	83
2	1694	31	1500	35	15	147	98
3	1694	31	1500	35	15	159	106
4	1694	31	1500	35	15	158	105
5	1694	31	1500	35	15	153	102
6	1694	31	1500	35	15	159	106
			6000	35		629	105
Proportions			1000				105
			952				100

A run of six days, with 1500 lbs. bleaching powder for each charge, was made with the result given in Table XIV.

Since the works ran smoothly, the contents of the apparatus not boiling over, and since still *B* was less than three-quarters filled at the completion of the charge, the larger charge was thought possible in the regular run, whereby the capacity of the plant was increased by 50 per cent.

In making this run it was observed that the first thousand pounds bleach made more chloroform proportionately than the following 500 lbs. In Experiments Nos. 3 to 6, 113, 116, 113, 116 lbs. washed chloroform, respectively, were obtained from the first thousand pounds bleach, 35 per cent., while 47, 40, 40, 45 lbs., respectively, were obtained from the following 500 pounds.

From this observation it might be concluded that greater concentration of alcohol would produce a still greater yield. But the advantage did not seem sufficiently large to justify the increased consumption of steam and the decrease of the capacity of the plant, and for this reason experiments in this direction were not carried on.

Following these runs, all six apparatus were changed in the same manner and they were operated parallel with bleaching powder, 31 per cent. to 37 per cent., for several years. From time to time, operations were discontinued to make calculations, or for other reasons, and the following are the results obtained from several lots. In every instance, the diluted alcohol obtained in the last operation was redistilled with calcium hydrate, and the amount of alcohol obtained was deducted from the amount of alcohol used in the aggregate operations, the difference being the alcohol, 94 per cent., used up for chloroform.

Record of a thirty-three days' run, with 35 per cent. bleach, showed the daily variations. On every day, except the thirtieth day, six apparatus were used, while on the thirtieth day only five were in commission, one being in repair. One and one-half casks bleach, 35 per cent., weighing about 1500 lbs., were used for a charge in each apparatus in every day's run except on the first day, when only one cask per apparatus was charged.

The diluted alcohol, coming from the last operation, contained 640 gallons alcohol, 94 per cent., and from

TABLE XV.

Day No.	Bleach 35 per cent., used	Alcohol, 94 per cent., used.	Chloroform, s. g. 1.48, obtained	1000 lbs. bleach, 35 per cent., made chloroform
	Lbs.	U. S. gal.	Lbs.	Lbs.
1	6,322	559	510	81
2	9,055	90	940	103
3	9,160	120	959	104
4	9,011	120	931	103
5	9,196	90	968	105
6	9,125	120	942	103
7	9,075	120	949	104
8	9,503	90	1,039	109
9	9,268	90	967	104
10	9,206	90	930	101
11	9,100	90	943	104
12	9,221	120	924	100
13	9,172	120	954	104
14	9,157	120	987	108
15	9,274	120	1,001	108
16	9,240	120	927	101
17	9,254	120	967	104
18	9,352	90	942	100
19	9,160	120	969	105
20	9,263	120	1,001	108
21	9,146	90	977	106
22	9,107	120	1,016	101
23	9,311	90	984	105
24	9,327	120	985	103
25	9,106	120	1,029	103
26	9,154	90	970	106
27	9,207	120	968	105
28	9,140	120	957	105
29	9,072	100	949	105
30	7,576	120	838	100
31	9,632	90	1,013	105
32	9,047	120	993	100
33	9,556	152	990	103
	299,525	4,081	31,419	105

the 31,419 lbs. washed chloroform, 30,675 lbs. pure chloroform were obtained. The net result of the run was, therefore, that 299,525 lbs. bleach, 35 per cent., and 3441 gallons alcohol, 94 per cent., made 30,675 lbs. pure chloroform, which is equivalent to 102.4 lbs. pure chloroform from 1000 lbs. bleach, 35 per cent., and 11.49 gallons alcohol, 94 per cent., or 100 lbs. pure chloroform required 977 lbs. bleach, 35 per cent., and 11.22 gallons alcohol, 94 per cent.

Record of 8 lots chloroform, made from bleach containing 31 to 37 per cent. chlorine and alcohol, showing variations by different strengths of bleach:

TABLE XVI.

Lot.	Bleaching powder used. Bought for		Equal to		Alcohol, 94 per cent., used.	Chloroform obtained. Crude, s. g. 1.48.	Pure.
	Per cent.		Per cent.				
No.	Lbs.	Cl.	Lbs.	Cl.	U. S. gal.	Lbs.	Lbs.
1	353,375	32	323,085	35	3,710	30,155	29,446
2	53,968	32	49,342	35	536	4,244	4,046
3	185,414	35	185,414	35	1,930	16,065	15,982
4	299,525	35	299,525	35	3,441	31,419	30,675
5	168,178	31	148,958	35	1,732	15,373	14,925
6	83,218	37	87,973	35	880	8,279	8,182
7	577,871	35	577,871	35	6,646	62,595	61,124
8	799,387	35	799,387	35	9,013	77,916	77,551
			2,471,555	35	27,888	246,046	241,931
Proportions....			1,000	35	11.28	99.5	97.9
			1,022		11.53		100.0

Comparing this with the results obtained by the old process and recorded in Table I, a saving of 0.20 gallon alcohol, 94 per cent., and 415 lbs. bleaching powder, 35 per cent., was effected for every 100 lbs. of chloroform made by the new process.

The saving in alcohol was insignificant, but there was no saving expected, the experiments indicating the consumption of 11.5 gallons alcohol for every 100 lbs. of chloroform, while 11.53 gallons were used in actual work. The gain in bleaching powder, however, was 29 per cent., quite near to the 34 per cent. saving, which were indicated by the most favorable experiments in Series N. The consumption of steam was larger than in the old process, since about 400 gallons diluted alcohol were to be distilled off in each operation, in order to recover all the alcohol. About 3 tons steam were required for each apparatus in a day's work. However, 1500 lbs. bleach could be worked daily in each of the six stills, in place of 1000 lbs., and 147 lbs. pure chloroform were manufactured per day in each still, in place of 70 lbs., which could be made by the old process, an increase in capacity of the plant of over 100 per cent.

The amount of steam used by the new process was 2 tons for 100 lbs. chloroform, against 1.1 tons in the process, for the same amount.

The same number of laborers ran the improved plant, after mechanical washers had been installed, the same laborers making more than twice the former product.

There are localities in the western states where corn, limestone and salt are cheap, where coal and power are abundant. There may be a market for caustic soda but none for bleach, which cannot be disposed of on account of the freight rates. By making chloroform, many pounds of material can be condensed into one and can be shipped to the centers of population.

COMPARISON OF SOME METHODS FOR THE ESTIMATION OF SULFUR IN VULCANIZED RUBBER WITH ESPECIAL REFERENCE TO ELECTROLYTIC OXIDATION.

By D. Spence and J. Young.

Received Feb. 3, 1912.

This work was primarily undertaken in order to find a rapid and, at the same time, accurate method for the determination of combined sulfur in vulcanized rubber, applicable to samples containing widely different quantities of combined sulfur. A method such as this is well-nigh essential to a study of the kinetics of vulcanization such as we had in view where a large number of simple compounds of rubber and sulfur containing all percentages of sulfur from 0.5 to 32 per cent. had to be investigated. Previous experience in the determination of the sulfur of vulcanization had shown that a method which might be applicable to one compound was not necessarily equally applicable to every other. This was a condition, however, which we had to meet in our work and it is one which is of importance in the every-day analysis of vulcanized rubber.

In view of the ever-increasing importance of methods for the chemical analysis of India rubber and the attention which is being directed towards this subject by committees appointed here and abroad, this present work should be of interest not only as furnishing the solution to our specific problems, but as offering to those engaged in the analysis of India rubber a method for the determination of sulfur at once simple, rapid and accurate, which has not yet received that recognition in this country which it undoubtedly merits.

This is not, and does not pretend to be, a complete study of all the methods which have been published in the literature from time to time for the determination of sulfur in India rubber. We have dealt here only with those methods which, from previous experience or from other reasons, seemed likely to meet the requirements of our work and our attention has, therefore, been confined to a comparative study of the methods of Carius, Henriques (methods involving fusion) and Gasparini (electrolytic oxidation) and to modifications of these by ourselves and others.

The Carius method requires no description here. It has long been recognized as an accurate one for the determination of sulfur in vulcanized rubber and we believe it is still in very general use where the highest accuracy is required. The disadvantages to the method are as well known, however, as the method itself. We need only refer, for example, to the cumbersome and altogether precarious nature of the work involved in the process which even the modifications investigated by us have not succeeded in eliminating. Similarly, the old method of Henriques[1] for the determination of sulfur in rubber and the methods of Frank and Marckwald,[2] Wagner,[3] and others, which are only slight modifications of the former, although perhaps simpler in some respects than the Carius method, require time and attention if reliable results are to be obtained, which, for our work at least, was out of the question. The fusion, namely, of the products of oxidation of the rubber by nitric acid, we have found to be so delicate and precarious an operation, even when carried out by the modified method described in the experimental part of this paper, that if constant care and attention is not given results of very uncertain value may be obtained. Our experience with methods of fusion indeed has been that in the long run more time is involved and less assurance of accuracy in the final result obtained than by a modified Carius method. There is little, if any, advantage, therefore, in fusion methods over Carius methods.

Far more interesting, however, than either of these methods is that of electrolytic oxidation. Of all methods for the estimation of sulfur in India rubber investigated by us, this method proved not only the simplest but also the most reliable. Not only is it unequaled in these respects, but we have found it applicable, and without modification, to the determination of the sulfur in rubber of any degree of vulcanization.

The method was originally evolved by Gasparini[4]

[1] *Z. angew. Chem.*, **34**, 802 (1899).
[2] *Gummi Zeitung*, **17**, 71 (1903).
[3] *Ibid.*, **21**, 552 (1907).
[4] *Gaz. chim. ital.*, **37**, II, 426-461 (1907).

for the estimation of sulfur in organic compounds, including vulcanized rubber, and recently has been made use of by Hinrichsen[1] in his work on vulcanization.

The method is an exceedingly accurate one. Indeed, in view of its simplicity and at the same time its accuracy, doing away as it does with all the objectionable features of other methods, it is surprising to us that it has not received more general application. We can only recommend it to the attention of those engaged in the analysis of vulcanized rubber.

To meet the case of complex rubber mixings the method is subject to the same modifications as are common to all existing methods.

In conjunction with a form of volumetric process for the determination of sulfur such as the barium chromate method[2] investigated by us, or the benzidine method of Raschig,[3] we believe the process is capable of still further simplification to meet the requirements of a still more rapid and accurate method for the determination of sulfur in soft-cured rubber. Complex mixings would, of course, require special attention where the volumetric process using barium chromate is introduced. It is only, however, by practical work directed towards the solution of just such problems as these that real progress towards standard methods of analysis of rubber can be hoped to be made.

EXPERIMENTAL PART.

At the outset of this work it was necessary to adopt a standard method of analysis to which all our work could be referred. The Carius method was selected for this purpose in spite of the fact that the values obtained by it are stated to be slightly too high[4] on account of the inclusion in the precipitated sulfate of a very small quantity of silica dissolved from the glass. The error by this method we have found to be very small, however, and constant, if reasonable care is taken. In all our work, therefore, unless otherwise stated, our figures for sulfur are compared with those by the Carius method.

In carrying out the Carius method it has long been customary here to modify the original procedure to the extent of effecting the preliminary solution of the rubber in the acid in a closed bomb at as low a temperature as possible, afterwards opening the tube and heating it on the steam bath until further vigorous action ceases, then resealing the bomb and completing the oxidation by heating the tube to 170° C. for 3 hours. In this way the intense gaseous pressure which is generated in a closed bomb by the first action of nitric acid on India rubber is relieved and the complete oxidation of the rubber takes place under conditions which, while preventing loss of sulfur, are less likely to bring disaster to the estimation by the bursting of the bomb in its final heating.

[1] *Koll. Zeitsch.*, **8**, 248 (1911). The statement by Waters and Tuttle, THIS JOURNAL, **3**, 734 (1911), that this method is due to Hinrichsen is, therefore, incorrect. Gasparini has shown how the method may be applied to the oxidation of vulcanized rubber.

[2] *Amer. Chem. Jour.*, **2**, 567 (1880).

[3] *Z. angew. Chem.*, **1903**, 617 and 818. See Sutton's "Volumetric Analysis," 10th edit., p. 353.

[4] Anelli, *Gaz. chim. ital.*, **41**, I, 334.

In this modified form the Carius method has been found to be safer and less troublesome than the ordinary Carius process when applied, in particular, to samples of vulcanized rubber having a high content of rubber. The method has been tested by us against the standard Carius method, in which the rubber is first brought in contact with the acid in a closed bomb and is heated before the pressure is relieved, and has been found to give satisfactory results. A comparison of results obtained by this method against those obtained by the electrolytic process will also be found in the section on electrolytic oxidation, which follows.

In the modified method just described the Carius process still, however, remains tedious and somewhat precarious. To further simplify it an experiment was made in which the rubber was added directly but slowly, small pieces at a time, to the acid in the bomb which was warmed or cooled as required in order to complete the solution of the rubber without a too vigorous action ensuing. In this modification, therefore, the preliminary solution and heating took place in *open* bomb. A sample of hard rubber analyzed in this way gave 31.60 per cent. of sulfur as against 31.50 per cent. by the ordinary Carius method. This method of treatment is somewhat simpler and apparently gives accurate results. Even with this modification, however, the Carius method is cumbersome where many sulfur estimations have to be made.

More promising, at first sight, as a rapid method for the determination of sulfur in vulcanized rubber, appears the process of fusion with alkaline oxidizing agents. This process, in its simplest form, consists in the fusion of an intimate mixture of the finely ground material with an excess of powdered sodium carbonate or a mixture of sodium carbonate with potassium nitrate. Such a method has recently been applied with success[1] by one of us to the determination of bromine in the tetrabromide of India rubber and was found to give reliable and satisfactory results in this connection. The process is exceedingly simple. In our efforts to apply it to the determination of sulfur in vulcanized rubber we were confronted, however, with the difficulty of obtaining intimate mixture of the sample with the alkali fusion mixture. Sulfur values were always lower than those by the Carius method. Even in the case of a sample of finely powdered, hard rubber dust, where intimate mixture of the dust with the alkali was possible, 17.53 per cent. of sulfur was found by this method as against 30.80 per cent. by the Carius method. One can only conclude from this that the chemical combination of rubber and sulfur to hard rubber is much more stable towards alkaline oxidizing agents than the corresponding bromine derivative of India rubber. Some incineration experiments carried out, using Eschka's mixture directly, proved equally unsuccessful for similar reasons.

The root difficulty in direct fusion methods as applied to vulcanized rubber undoubtedly lies in obtaining intimate mixture of the rubber material with

[1] *Le Caoutchouc et la Gutta Percha*, **8**, 88, 5313 (1911).

e fusion mixture. It was to overcome this fficulty that Henriques[1] evolved the method of st dissolving the rubber in nitric acid, taking the lution thus obtained to syrupy consistency before ixing with the fusion mixture. This is a great adnce over simple fusion, and with care and attention e old method of Henriques has been found reliable the hands of experienced analysts. For the sake a comparison we made a number of estimations by e Henriques and our modified Carius method on mples of vulcanized rubber having widely different lfur content. The Henriques method was card out by us in the modified form as described by ank and Marckwald.[1] The results obtained by e two methods are given in tabular form in Table I.

TABLE I.

Method.	Total sulfur. Per cent.	Combined sulfur. Per cent.	Total sulfur. Per cent.	Combined sulfur. Per cent.	Total sulfur. Per cent.	Total. sulfur. Per cent.
Carius method.....	13.14	3.95	22.73	5.21	8.04	4.59
Henriques method..	12.97	3.67	21.65 22.17 22.50	5.08 5.05	7.97	4.44

The results are not as satisfactory as we had hoped ey would be. Our practical experience with the ethod, besides revealing to us that it is excessively mbersome and altogether unsuitable for the work we d in view, showed that it still contains one cardinal eakness which the treatment with nitric acid in the rst instance does not overcome. The treatment, amely, of the rubber by nitric acid results in the formaon of nitro derivatives of the rubber ("nitrosites") hich on fusion with alkali will sometimes cause urting and small explosions with loss of sulfur en when the utmost care and constant attention given to the fusion process. The results by the ethod are usually low in consequence. The trouble s largely in the fact that it is well-nigh impossible obtain a uniform mixture of the syrupy products decomposition of the rubber by nitric acid with e solid alkaline mixture.

We lay no claim to be the first to draw attention this inherent weakness in the Henriques fusion ocess. To overcome it, Wagner[2] has suggested e diluting of the syrup obtained by treatment of e rubber by nitric acid with water, rendering the ueous solution thus obtained faintly alkaline by ans of solid KOH and afterwards concentrating half bulk before mixing with excess of sodium carnate and fusing. The underlying idea we believe be a happy one. We have gone further, however, id have modified Henriques' method to the extent mixing the products of oxidation of the rubber by ric acid with the alkaline fusion mixture in solun, afterward taking the whole to dryness prior to ing. In this way complete and thorough mixing the products of oxidation of the rubber with the ion mixture is effected and the subsequent fusion h be readily carried out without much difficulty or danger of loss due to ignition of the mixture. The method as carried out by us was as follows:

The rubber is dissolved in a mixture of 10 cc. fuming HNO_3, 5 cc. H_2O and 3 g. KNO_3 with cautious warming, if necessary, to start the reaction. The solution obtained is evaporated almost to dryness, the residue dissolved in a solution of 6 g. Na_2CO_3 in 15 cc. H_2O, thoroughly mixed with same, and again taken to dryness. The drying of the mixture and subsequent fusion are carried out with the usual precautions:

Results.	Modified Henriques. Sulfur found. Per cent.	Carius. Sulfur found. Per cent.
I.	31.26	30.80
II.	23.07	23.34

That no great loss occurs in the process of fusion as carried out by us was shown by an experiment in which the rubber was dissolved in fuming nitric acid and water as above and the solution afterwards made up to a known volume (50 cc.) with fuming nitric acid. One-half of this standard solution was treated by our modified Henriques method while the sulfur in the other portion was determined by Carius:

	a. By fusion. Per cent. S.	b. By Carius. Per cent. S.
Results.....	31.09	31.22

Some experiments on the modified Henriques method, using nitric acid saturated with bromine, as recommended by Waters and Tuttle,[1] were also made.

The results are given in the following table and in comparison with the values by Carius are, on the whole, satisfactory:

Method.	Sample I. Combined S. Per cent.	Sample II. Combined S. Per cent.	Sample III. Combined S. Per cent.
Modified Henriques (Waters and Tuttle).....	3.01	10.93	31.47
Carius.....	3.05	11.28	31.44

The experience derived from our study of the methods of fusion outlined above showed, however, that although accuracy can be obtained by these methods, great care and constant attention is required if they are to be reliable in every instance. Even the best of them are cumbersome and are not adapted to rapid and at the same time accurate work. This is an important point where the accurate estimation of sulfur in India rubber is a routine laboratory operation.

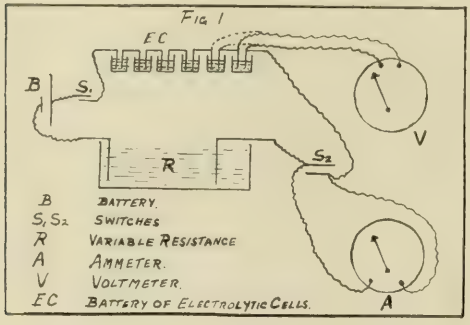
Very different, on the other hand, were our experiences with the electrolytic process of decomposition. This process, originally designed by Gasparini[2] for the estimation of sulfur in organic compounds in general, depends on the decomposition of the organic substance by nitric acid in presence of an electric current. Gasparini designed a somewhat complicated apparatus to carry out the oxidation of the organic substance without loss of sulfur. We have found, however, that as far as the sulfur of India rubber is concerned, any complication of this kind is unnecessary and that accuracy can be obtained by very simple means. In the early stages of our work on this method we were confronted, as was to be expected, with difficulties, difficulties not confined,

[1] *Loc. cit.*
[2] *Gummi-Zeitung*, **21**, 552 (1907).

[1] THIS JOURNAL, **3**, 10, 734 (1911).
[2] *Loc. cit.*

however, to this method only, but these disappeared one by one as we became better acquainted with the method so that in the form in which we now present it, the method can be readily carried out even by the inexperienced.

The sample of rubber weighing about 0.5 gram[1] is put into a tall 500 cc. Jena glass beaker and covered with concentrated HNO_3 (sp. gr. 1.4). The beaker is covered by a clock glass and is then very gently warmed on the steam bath. As soon as the reaction starts the beaker is removed from the steam bath and the solution allowed to continue without further heating. If too much heat is applied at the beginning, it may be necessary to put the beaker in cold water in order to moderate the reaction. In about 2–3 minutes the solution of the rubber is complete and all frothing of the liquid ceases. To this solution is now added 30 cc. of fuming nitric acid (sp. gr. 1.5) with which the clock glass is washed. A current of electricity is now passed through the solution between electrodes of platinum foil. The most suitable current is 3 amperes with a potential of 6–8 volts between the electrodes. The electrical connections are made as shown in the diagram (Fig. 1).



The current may be taken from any d. c. source and if necessary is reduced by means of a variable resistance, R. The ammeter A is shunted at the terminals of the switch S_2 so that by opening the switch it is thrown into the circuit. The voltmeter V is introduced between the terminals of the electrodes. Any number of estimations may be connected up in series, the voltage in each cell being tested separately. The time required for the complete oxidation of the rubber varies with the sample. For soft-cured rubber containing a high percentage of rubber we have found that 2 to 3 hours are required. With hard rubbers containing a lower percentage of rubber the oxidation is complete in $^3/_4$ to 1 hour. At the end of the action the electrodes are removed and washed with water. About one gram of pure Na_2CO_3 is then added and the solution evaporated to dryness on the steam bath. The residue is moistened with conc. HCl and taken to dryness again. The residue which should be free from nitric acid and nitrates is dissolved in hot water, filtered if necessary from insoluble matter and the sulfur precipitated as barium sulfate in the usual way.

The solution of the rubber, when carried out as described, proceeds smoothly and without difficulty. The electrolysis, when the current and voltage have once been determined, proceeds quietly and requires no attention whatsoever on the part of the operator. The final stage of the process is common to all methods for the determination of sulfur where nitric acid is used and requires no criticism here.

In order to still further simplify the method the apparatus shown in Fig. 2 was designed by us. This

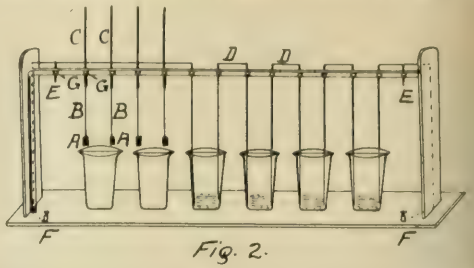


Fig. 2.

apparatus enables six estimations to be carried out at one time and does away with all binding screws and cumbersome connections—a very desirable feature, particularly where nitric acid is in constant use.

The decomposition of the sample is carried out in beakers as before. These are the regular "high form type" of beaker of Jena glass and have the following dimensions approximately: Height 100 mm., diameter 55 mm., capacity 200 cc. The beakers are covered by clock glasses split in two in order to admit of the wires carrying the electrodes. The electrodes A are of platinum foil (one sq. inch in area) riveted to a piece of platinum wire, B. The free end of the wire is fused into a glass tube filled with mercury. The glass tubes slide in grooves cut in the cross support, and the electrodes can in consequence be fixed at any height by means of the wooden binding screws G,G. Connections are made by means of small bridges of copper wire, D, dipping into the mercury in the glass tubes. The binding screws F,F are connected by means of a wire with the mercury cups E,E. With the connections arranged in this way it is a simple matter to remove or introduce an estimation at any stage, connection being made across the gap with a double-length bridge.

If the dimensions and quantities specified above are adhered to, a determination of the potential difference between the electrodes of each cell becomes unnecessary in each estimation, for, with the electrodes placed at the extreme circumference of the beaker, opposite one another and completely immersed in the acid, we have found that the required voltage is at once attained with sufficient accuracy for the purpose of the estimation.

The reaction in the cell, which is fairly vigorous at first giving rise to a considerable evolution of heat, soon moderates and when decomposition is complete almost ceases, the potential difference meantime falling gradually.

Some results of analyses of products of different degrees of vulcanization are given in the following table. These show the applicability of the method to the analysis of rubber of all degrees of vulcanization:

Method	1. Sulfur found. Per cent.	2. Sulfur found. Per cent.	3. Sulfur found. Per cent.	4. Sulfur found. Per cent.	5 Sulfur found. Per cent.
Electrolytic oxidation.....	1.27	3.02 3.11	4.19	11.35 11.39	31.39 31.39
Carius.....	1.32	3.05	4.27	11.28	31.44

[1] More may be conveniently used where the sulfur content of the sample is very low.

The method of electrolytic oxidation is now in regular use here. A great deal of work has recently been carried out by means of it where both total and combined sulfur in vulcanized samples of rubber mixings had to be determined. These results have not only served to establish beyond all doubt the accuracy of the method but they have shown that it leaves little to be desired in the way of a simple process for the determination of sulfur in India rubber.

By introducing a volumetric process for the determination of the sulfur we have found it possible to still further simplify this method. We have found, namely, that the Pennock and Morton[1] rapid process for the determination of sulfur in coal and coke can be advantageously employed where the variation in the amount of sulfur present in different samples is not great.

This process depends on the decomposition of barium chromate by sulfuric acid, the liberation of iodine from potassium iodide in acid solution by the chromic acid set free and the titration of the iodine liberated by sodium thiosulfate. 1 cc. $N/10$ thiosulfate is equivalent to 0.001067 gram sulfur.

A rigorous investigation of this process was first made on standard solutions of potassium sulfate of different concentration. We will refrain, however, from quoting our results in this connection. The method was found to be satisfactory where the sulfur present did not vary within wide limits. Several analyses of India rubber were then carried out by this method and checked against the ordinary gravimetric process. Results:

Volumetric. Per cent. S.	Gravimetric. Per cent. S.
1.602	1.43
3.38	3.29
22.31	23.34

Only the results of the lower values are in agreement with the gravimetric figures. In carrying out this process one of the first essentials appears to be that the sulfuric acid and excess of barium chromate used in each experiment shall be as nearly as possible constant quantities. This is a comparatively easy matter to arrange where, as in the case of normal cured soft rubber, the sulfur does not usually exceed 5–6 per cent. and is a fairly constant quantity. But when, as in the examples cited, the variation is great and the correction to be applied is unknown and a constantly varying quantity, errors arise in the volumetric process. That it is impossible to overcome this difficulty by selecting a suitable weight of sample for analysis is fairly evident. This is not always an easy matter, however, where the sulfur content of the sample may vary between 0.5 per cent. and 32 per cent. In our work, therefore, in the meantime, we have adopted the gravimetric process until the foundations of the volumetric method shall have been more fully investigated.

[1] *Jour. Am. Chem. Soc.*, **25**, 1265.

A METHOD FOR DETERMINING THE VALUE OF COMMERCIAL STARCHES FOR USE IN COTTON MILLS.

By G. M. MacNider.

Received Jan. 16, 1912.

In the manufacture of all grades of cotton cloth the yarn is prepared for the loom by a process known as sizing, in which it is treated with a solution of starch to give it certain properties essential to good weaving. With many grades of cloth, the cloth goes through a process known as finishing, where it is again treated with starch to produce a "finish" before it is put on the market. It is thus seen that the cotton mills use annually large quantities of starch and the purchase of the best starch for the purpose in hand becomes a very important matter.

The value of starch for cotton mill purposes depends on its property of swelling and forming a viscous solution when treated with hot water. It is the purpose of this paper to give a method for determining the viscosity of starch solutions which will show the comparative value of the different starches for use in cotton mills. The sizing and finishing of cotton goods are very technical operations and will not be taken up in detail. Sufficient reference will be made to them to show the function of the starch solution.

The object of sizing is to make the yarn stiffer, increase the strength and put it into proper condition for weaving. To accomplish this, the size must penetrate the yarn to some extent and also form a coating on the surface of the thread, which prevents wear of the thread in the loom. The size is prepared by boiling the starch (and other ingredients) with water and is applied to the yarn while hot. The machinery is so constructed that the threads are dried immediately after passing through the size.

The object of finishing is to give a stiffness to the cloth and produce a certain finish and "feel" which are very important factors in marketing cotton goods. As in sizing, the cloth is passed through a hot solution of the finish and then dried and rolled with hot rollers to bring out the finish. The use of the starch solution alone in these operations would make the goods too stiff and produce a harshness which is not desirable. To modify this, various softening agents are used, *viz.*: tallow, various oils, soaps, magnesium chloride, magnesium sulfate, glycerine, etc., and in many mills various sizing and finishing preparations.

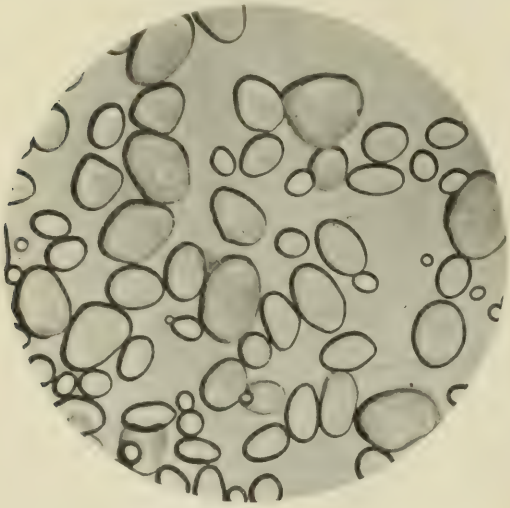
The principal starches used by the cotton mills are corn, potato, cassava, and to a small extent wheat, sago and rice. In England, wheat flour and rice flour are used to a considerable extent, but in America they are used very little. As will be seen later, each one of these starches has a different viscosity and therefore must be used in a different manner. Some authors attribute the differences in the characteristics of the starch solutions to the size and shape of the starch grains. There is no definite relation existing to prove this. The appearance of the different starch grains under the microscope are shown in the following cuts.[2]

A number of methods have been proposed for determining the viscosity of starch pastes, but in none of them has an attempt been made to determine the viscosity of the starch under conditions similar to those under which it is used in the cotton mills; conse-

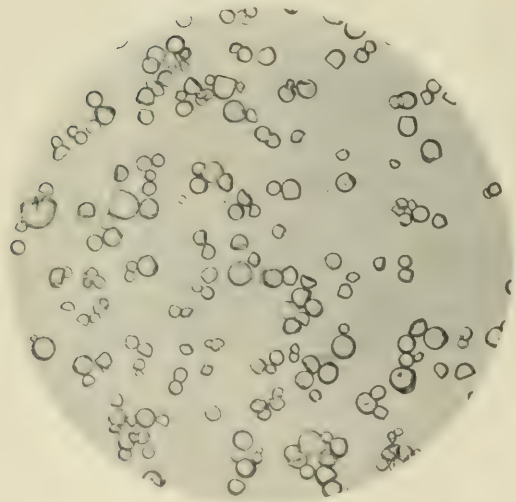
[2] These cuts were very kindly furnished the author by Mr. B. J. Howard, of the Bureau of Chemistry, Washington, D. C.

quently they do not show the value of the starches for these purposes. Following is a brief description of the methods which have been proposed:

Whewell[1] uses a method for determining the viscosity of starch pastes which depends upon measuring the ability of thick pastes, made of definite amounts of starch, to support a known weight for a definite length of time. This method is a measure of the strength of the film formed on the surface of the paste



Potato Starch × 200.



Cassava Starch × 200.

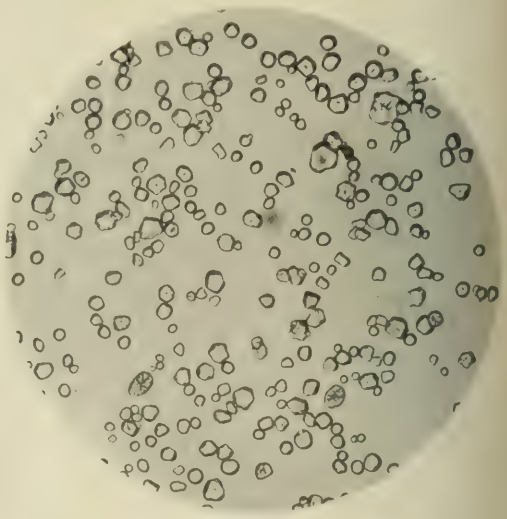
and is not a measure of the viscosity; it frequently gives results which are the reverse of actual viscosity measurements.

Saare[2] and Martens propose a method, the essentials of which are making in a beaker a paste of definite weight and immersing in it a brass disc attached to a wire; the disc is supported at a definite point in the paste and the whole allowed to stand for 20 hours at 17.5° C.; by means of a balance attached to the disc, the weight required to draw the first weight out of the paste is then measured and the last weight is taken as an indication of the viscosity of the starch.

Benz[3] and Marx propose a method for determining the stiffness of starch paste which is very similar to the one given by Saare and Martens.

Coppenberg[3] describes a viscosimeter for starch pastes in which a spherical weight is drawn upwards through a column of the paste of fixed height and temperature. The time in seconds occupied in doing this, under the pull of a known load in grams, constitutes an observation. The apparatus is adaptable only to thick liquids.

Ermen[3] proposes a method for determining the viscosity of starch in which the starch paste is made by treating the starch with a solution of sodium hydroxide. The paste is allowed to stand for a certain length of time and the viscosity determined in a Redwood viscosimeter.



Corn Starch × 200.

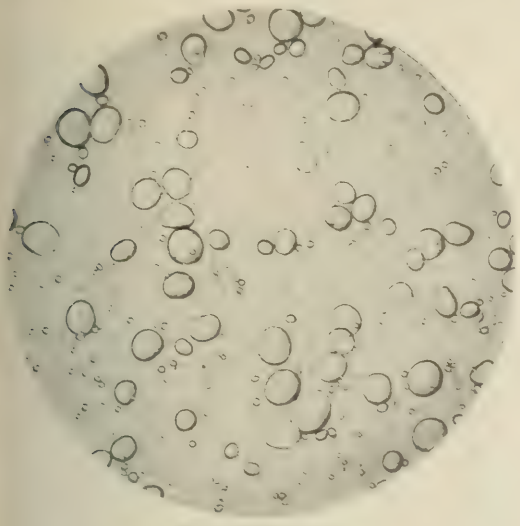
The use of alkali in making the paste prevents this method from being a measure of the viscosity of the starch, as the paste formed by treatment with alkali has entirely different properties from the straight starch paste.

Bean[4] gives the following method for testing the consistency of wheat flour and starches. The samples are placed in beakers with the proper amount of water; the beakers are immersed in boiling water, allowed to remain 15 minutes, removed and allowed to cool for 12 hours. A sample of the standard starch or flour to be used for comparison is treated in the same manner. "Any variation in the consistency may be judged by pressing the fingers into each sample."

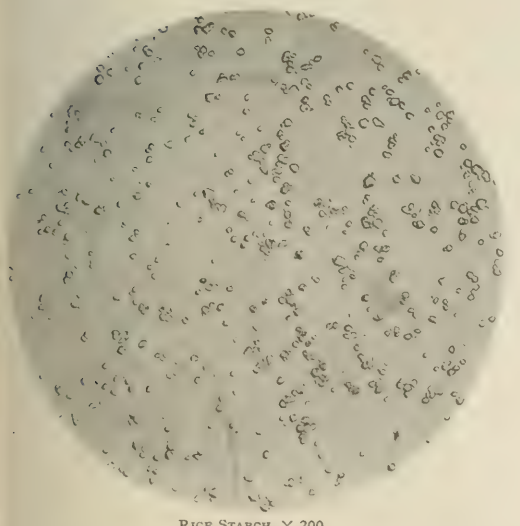
[1] *Chem. News*, **39**, 97.
[2] *Zeits. Spiritusind.*, **26**, 1903; Abs. in *J. Soc. Chem. Ind.*, **22**, 1903.
[1] *Chem. Ind.*, **32**, 1909; Abs. in *J. Soc. Chem. Ind.*, **28**, 1909.
[2] *Chem. Zeit.*, **34**, 1910; Abs. in *J. Soc. Chem. Ind.*, **29**, 1910.
[3] *J. Soc. Chem. Ind.*, **26**, 1907.
[4] "The Chemistry and Practice of Sizing."

In both sizing and finishing the starch is boiled with water for a certain length of time and the solution applied to the yarn or cloth at a temperature a few degrees below boiling. The temperature is not allowed to fall below 70° C. and is usually maintained at about 90° C.

These methods do not test the viscosity under conditions similar to those under which the starch is used in the mills, and consequently no deductions can be made from the results as to the value of the starches for mill purposes.



WHEAT STARCH × 200.



RICE STARCH × 200.

In the following method the starch solution is prepared by boiling the starch with water for a definite length of time and the viscosity of the hot solution is measured by means of a Scott viscosimeter. In this way the viscosity of the starch solution is obtained under conditions practically identical with those under which it is used in the mill.

Before starting the determination, the viscosimeter bath should be filled with water which is kept boiling throughout the operation. The method is as follows:

Twelve grams of the starch are weighed into a 600 cc. beaker, 300 cc. distilled water added (thus making a 4 per cent. solution) and heated over a Bunsen burner with constant stirring to the boiling point and boiled for ten minutes; 200 cc. of this solution are then poured into a viscosimeter cup, the temperature allowed to become constant, and 50 cc. run out into a graduate, the time being accurately measured with a stop watch. The number of seconds required to deliver 50 cc. of the solution divided by the number of seconds required to deliver 50 cc. of boiling water gives the viscosity.

Before the starch is weighed out it should be thoroughly pulverized to remove the lumps. During the heating and boiling it is very necessary that the solution be constantly stirred to prevent the formation of lumps and caking on the bottom and sides of the beaker. Glass beakers break so easily in boiling the heavy solutions that aluminum beakers were substituted and used for all determinations.

A number of determinations were made at first to determine the best amount of starch to use and the necessary length of time to boil the solution. It was found that a four per cent. solution of starch was the most satisfactory strength to use. With thin boiling starches this strength solution is heavy enough to measure the viscosity satisfactorily while the starches forming thick solutions are not too heavy to interfere with the accuracy of the determination. With potato and cassava starch it would be practically impossible to obtain accurate results with a stronger solution. Ten minutes was decided upon as the best length of time for boiling, as this is long enough to develop the characteristics of the starch and at the same time the solution has not been effected by loss from evaporation. The temperature at which the determinations were made was the temperature which the boiling solutions assumed on being poured into the viscosimeter cup, the viscosimeter cup being surrounded by boiling water. With most of the starches this was 94° C. With rice starch the temperature fell to 92.5° C. It was found that at such high temperatures a variation of one or two degrees does not appreciably effect the viscosity, though at lower temperatures a variation of less than a degree produces a marked effect. In all determinations checks were obtained which did not show a variation greater than two-fifths of a second and most of them checked within one-fifth of a second. With the viscosimeter used, the time required to deliver 50 cc. was 9 seconds. This figure was used in calculating all determinations.

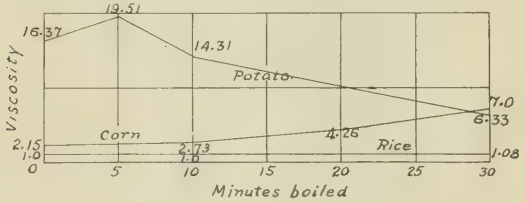
The following table shows the viscosity of the starches examined and the variation in the viscosity of different lots of the same kind of starch:

VISCOSITY OF COMMERCIAL STARCHES

1% grams starch in 100 cc water boiled 10 minutes

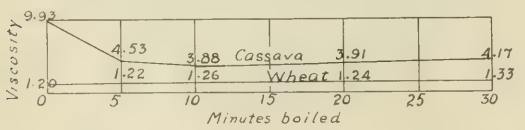
No.	Starch.	Seconds to deliver 50 cc	Viscosity.
510	Corn	22.4	2.49
508	Corn	25.8	2.86
521	Corn	24.6	2.73
502	Potato	128.8	14.31
524	Cassava	35.0	3.88
526	Cassava	35.8	3.97
527	Wheat	11.4	1.26
525	Wheat	11.2	1.24
528	Rice	9.0	1.00

From the above table it is seen that there is a wide variation in the viscosity of the commercial starches and consequently an equally wide variation in their value for mill purposes. It will be noticed that there is a considerable variation in the viscosity of different samples of the same starch. This may be due to several factors: the maturity of the plant from which the starch is made, the method used in manufacture and the manner in which the starch is dried; the latter will effect the amount of moisture in the starch. Starches of the same kind with different moisture content will show a variation in viscosity. This variation will be small unless the variation in moisture content is very large. While no attention is paid to the viscosity at present, it would be very



advantageous to the mills for each lot of starch (of the same kind) to have a uniform viscosity. This would enable them to obtain the same results in sizing and finishing without changing the formula for each lot of starch. By the above method a very small variation in the viscosity of a starch may be detected.

In practice the starch solution is boiled for a certain length of time before being used. To determine what effect this has on the viscosity of the solution, viscosity determinations were made at different periods of boiling with each starch. The results obtained are shown by the accompanying curves.



In boiling the starch solutions no attempt was made to keep the volume constant, as the addition of water to a starch solution materially reduces the viscosity. The loss from evaporation was practically the same with all solutions, and as they were carried out under the same conditions the results are comparable. In boiling rice starch 30 minutes the loss from evaporation was greater than with the other starches, but as this starch shows no change in viscosity on continued boiling this need not be considered.

From the curves it will be seen that the viscosity of corn starch increases uniformly with the length of time of boiling. This increase is about what would be expected with the concentration of the solution when there is no change in the starch. This is a very valuable property of corn starch as compared with other starches.

Potato starch reaches its maximum viscosity after being boiled five minutes. From this point the viscosity decreases rapidly with the increase in time of boiling, the concentration of the solution apparently having no effect on the viscosity. After boiling ten minutes, potato starch has a viscosity slightly more than five times as great as corn starch, while after thirty minutes the viscosity of potato starch is less than that of corn starch which has been boiled the same length of time. The author has found a number of references to the fact that potato starch "loses its strength" or liquefies on boiling, but has found no reference to the degree to which this takes place. The data given here show very strikingly the effect of boiling on this starch. Corn and potato starch form the two extremes in regard to this property.

Cassava starch attains its maximum viscosity at the boiling point. The solution apparently has a higher viscosity shortly after complete gelatinization takes place, but no measurements were made of this as starch is not used until it has been boiled. After reaching the boiling point the viscosity decreases uniformly with the length of time of boiling. After boiling thirty minutes there is an increase in the viscosity over that of the solution boiled twenty minutes. This increase is probably due to increased concentration. With both potato and cassava starch the solutions contain a good many air bubbles which sometimes interfere with the accuracy of the determination. As will be seen from the curve, cassava starch behaves in a manner very similar to potato starch as regards the liquefaction of the solution, but not to the same extent. Cassava starch therefore has a much broader application in sizing and finishing than potato starch.

Wheat starch has a much lower viscosity than any of the starches so far considered. It shows a gradual increase in viscosity with the time of boiling, similar to corn starch, though the total increase is small, the viscosity of the thirty-minute determination being only slightly higher than the determination made at the boiling point. Wheat starch foams more in boiling than any other starch.

Rice starch has the same viscosity as water. At the end of thirty minutes' boiling it shows only a very slight increse in viscosity.

It is a fact that starch goes into solution on continued boiling, that is, it is converted into soluble starch. The degree to which this takes place varies with the different starches. This is the only way of accounting for the marked differences in the viscosities of the various starches. Why the rate of solution should be so high in potato and so low in corn

is not known. It is a remarkable fact that the starches from roots and tubers, developed under ground, potato and cassava, show a high rate of solution while the starches from the grains, developed above ground, corn, wheat and rice, show a very low rate of solution.

SPECIAL OR TREATED STARCHES.

A number of starches are now used which are sold under a trade name, the advantages claimed for them usually being that they are "thin boiling starches." These are usually corn starch, which has been treated in some way to reduce the viscosity. The viscosities of six such starches are shown in the following table:

VISCOSITY OF SPECIAL OR TREATED STARCHES.
12 grams starch in 300 cc. water; boiled 10 minutes, temperature 94° C.

No.	Starch.	Seconds to deliver 50 cc.	Viscosity.
506	Eagle finishing.....	10.4	1.15
519	N starch, alkaline.....	19.2	2.13
511	Blue River, Pearl.....	19.2	2.13
529	Famous N.....	10.6	1.17
530	Thin boiling Crystal.....	11.2	1.24
531	Thin boiling Pearl.....	11.0	1.22

The Eagle finishing starch is corn starch treated with borax. The viscosity is less than half as great as that of straight corn starch. It will be seen from data given later that this starch has been treated in some manner other than the addition of a small amount of borax.

The N starch is corn starch made slightly alkaline. The alkalinity of this starch is equivalent to 0.001 gram of sodium hydroxide to each gram of starch. The viscosity of this starch is a few points lower than corn starch.

The other samples are treated corn starch, which are neutral and do not show any evidence of the way in which they have been treated.

Some determinations were made to ascertain the effect of several reagents known to be used in treating starches, on the viscosity of corn starch.

The effect of boiling corn starch with borax is shown in the following table:

EFFECT OF BORAX ON VISCOSITY OF STARCH.
12 grams starch in 300 cc. water, boiled 10 minutes; temperature 94° C.

No.	Starch.	Borax added. Gram	Seconds to deliver 50 cc.	Viscosity.
510	Corn.....		22.4	2.49
510	Corn.....	0.077[1]	19.0	2.11
521	Corn.....		24.6	2.73
521	Corn.....	1.0	26.0	2.86

From the data given, it is seen that a small amount of borax reduces the viscosity, but a slightly larger amount increases the viscosity. Bean[2] found that borax added to a thick starch paste while hot causes the sticky paste to lose its power of adhering to other substances and develop strong cohesive powers. The paste thus formed has the appearance of a jelly and may be rolled in the hands without any of it adhering to the hands. The properties of the starch are completely changed. The author has found a finishing preparation which is composed of starch treated with borax in this manner. Boric acid does not produce this effect.

[1] Amount of borax calculated from ash determination of No. 506.
[2] "The Chemistry and Practice of Sizing."

The effect of boiling corn starch with alkali is shown in the following table:

EFFECT OF ALKALI ON VISCOSITY OF STARCH.
12 grams starch in 300 cc. water; boiled 10 minutes; temperature 94° C.

No.	Starch	NaOH added. Gram	Seconds to deliver 50 cc.	Viscosity.
521	Corn	..	24.6	2.73
521	Corn.....	0.06	20.8	2.31

The amount of sodium hydroxide used was calculated from the alkalinity of the sample of N starch. From this it is seen that a very small amount of alkali produces a decided decrease in the viscosity. Some determinations were made using one-half of one per cent. of sodium hydroxide, but as soon as gelatinization took place the solution foamed so much that it was not possible to boil it. This excessive foaming would prevent the use of any considerable amount of alkali in sizing. The data obtained shows that a very small amount of alkali reduces the viscosity of starch, but a larger amount increases the viscosity.

In analyzing some sizing preparations it was found that boric acid was frequently used in them. Some determinations were made to determine the effect of boric acid on the viscosity of starch. The results are given in the following table:

EFFECT OF BORIC ACID ON VISCOSITY OF STARCH.
12 grams starch in 300 cc. water; boiled 10 minutes; temperature 94° C.

No.	Starch.	Boric acid added. Grams.	Seconds to deliver 50 cc.	Viscosity.
508	Corn.....	..	25.8	2.86
508	Corn.....	1	23.2	2.57
508	Corn.....	3	21.8	2.42
508	Corn.....	6	23.0	2.55

From this it is seen that a very small amount of boric acid reduces the viscosity, but when the amount is increased to as much as one gram of boric acid to two grams of starch the reduction in viscosity is not as great as when a smaller amount is used. If boric acid is used in sizing it should be used only in small amount.

It is often stated that some starches give a smooth finish to goods while others give a harsh finish. This property adapts the starches which produce a smooth finish for use on the finer grades of cloth which must have a smooth, soft finish, while the starches which do not produce such a finish are better adapted to the heavier grades of cloth. With most grades of cloth, no matter which one of the starches is used, some softening ingredient must be used with the starch to produce the desired result, and it is therefore more economical, in the majority of cases, to use a cheap starch and control the finish by use of softeners than to control the finish by varying the kind of starch used.

From the data which has been presented it is seen that the viscosity of the starch solution is the most important point to be considered in sizing and finishing cotton goods. As has been previously stated, to give satisfactory results the solution must penetrate the yarn or cloth and also form a coating on the outside. The viscosity does not show the stiffness which

will be given to yarn or cloth. This would be very difficult to determine, but it shows the comparative penetrating ability and the effect of boiling on the starches, and from this can be judged the effect which any given starch will produce on yarn or cloth. As there is so much difference in the viscosities of the several commercial starches it is very important for the manufacturer to use the starch which will give the most satisfactory results. When the costs of the different starches are considered this becomes a still more important matter. If, in sizing and finishing, the manufacturers will use only the kind of starch and softeners which are actually necessary to produce most economically the desired results, it will result in a great saving to all the mills engaged in this class of work.

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THE CHEMISTRY OF ANAESTHETICS, IV: CHLOROFORM.

BY CHARLES BASKERVILLE AND W. A. HAMOR.

Received December 13, 1911.

(Continued from May No.)

VIII. The Examination of Anaesthetic Chloroform.

1. THE TESTS FOR ODOR.

Pure anaesthetic chloroform possesses a characteristic odor,[1] and such chloroform volatilizes entirely without disagreeable or foreign odor. This property may be altered more or less by the presence of impurities, however, and this applies in particular to poorly rectified anaesthetic chloroform and commercial chloroform. The substances giving rise to a foreign or evil odor are the result of impurities present in the alcohol, acetone, etc., employed in the manufacture of the chloroform, or they are produced by various decompositions which occur; yet, as in the case of ethyl ether, there have been instances of sophistication, although these are now rare. There are more frequent cases of contamination resulting either from a lack of control in manufacture or from careless storage. We shall concern ourselves here with the impurities which are less volatile than chloroform, and which may consequently be recognized by evaporation tests.

About 1850, chloroform was found to be frequently contaminated with "oils" and in 1865, and thereabout, it was considered that "empyreumatic oils" were among the principal impurities of chloroform. It was known at this time that chloroform prepared from wood spirit was much less pure than that obtained from ethyl alcohol;[2] and that the first-mentioned was generally specifically lighter than chloroform made from alcohol, possessed a repulsive empyreumatic odor when crude, and, unless carefully purified, produced unpleasant sensations when inhaled.[3] It was learned that such chloroform was contaminated with approximately 6 per cent. of an "empyreumatic oil" containing chlorine;[3] and a similar oil was obtained by Soubeiran and Mialhe,[4] although in smaller quantity, in the preparation of chloroform from alcohol.[5]

About 1875 the presence of fusel oil in commercial chloroform was noted,[6] and it is likely that the anaesthetic chloroform in use from 1860 to about this time was generally contaminated with higher alcohols. A sample of anaesthetic chloroform made in 1863 was found by the authors to contain propyl alcohol.[7] Several even regarded the sickness following the use of chloroform to be due to the presence of amyl alcohol.[8] It was incorrectly pointed out that chloroform containing amyl or butyl compounds had a higher density than 1.500; and Gay[9] proposed a test for the presence of amyl alcohol based on odor.[10] The source of such contamination was both the impure alcohol used in the manufacture as well as that added as a preservative; and it was pointed out by Regnault and Hardy[11] that chlorinated compounds were formed by the action of bleaching powder on isopropyl, isobutyl, and isoamyl alcohols, and that, therefore, the alcohol used in the preparation of chloroform should not contain fusel oil.

In view of the possible contamination of anaesthetic chloroform with such substances, the value of a care-

[1] Passy (*Compt. rend.*, **116**, 769) made comparative experiments on the odorous power of chloroform, bromoform and iodoform, which afforded the following sharp results in millionths of a gram:

Chloroform	30.00
Bromoform	2–5
Iodoform	0.06–0.7

We may mention here that the odor of chloroform vapor may be masked by means of oil of cloves (Nussbaum, *Rundschau*, **1888**, 759), but more satisfactorily, from a medical standpoint, by the use of terpineol, for example. The authors, in conjunction with Dr. J. T. Gwathmey, have devised an effective means of masking the odor of both chloroform vapor and ether vapor; this method is now being used in practice.

[1] Ulex (*Year-Book Pharm.*, **1875**, 109) reported that certain chloroform conforming to all the requirements of the German Pharmacopoeia of that time was still unfit for medicinal use, and that upon the evaporation of a sample the residue developed an empyreumatic odor, resembling that of wood-spirit.

[2] Gregory (*Pharm. J.*, **9**, 580) considered that the unpleasant effect observed by Simpson and Carmichael in using one kind of chloroform was due to oily impurities. He stated that chloroform purified by means of sulphuric acid and then distillation over lime or barium carbonate, contained traces of "oils."

[3] This was found to burn with a smoky flame, to be lighter than water and to boil between 85° and 133° C.; this oil, it was learned, could not be completely separated by simple rectification, but it was found to be nearly destroyed by distillation with sulphuric acid.

[4] *Ann. chim. pharm.*, **71**, 225

[5] 20 kg. of chloroform from alcohol (presumably crude) were found to yield, when rectified over a water bath, 40 grams of oil residue; this was heavier than water, had an odor differing from that of the oil from wood-spirit, and possessed a boiling point varying from 68° to 117° C. Pemberton (*Pharm. J.*, **12**, 599) considered that Soubeiran and Mialhe had erred in describing the oily substance as a chlorinated oil; he believed it to be a mixture of paramylene and metamylene, with possibly traces of amylene, and that the slight volatility would prevent injurious effect during inhalation.

[6] Rump, *Archiv. Pharm.*, October, 1874.

[7] In Section IX, of this paper, the results of the examination of this sample will be given.

[8] For example, Martindale (*Pharm. J.*, [3], **12**, 734) and Werner (*Archiv. Pharm.*, [3], **12**, 481). Werner rectified about 5 kg. of chloroform and found in the residue a small quantity of a substance resembling fusel oil in odor. Valeric acid was obtained on distilling the residue with sulphuric acid and potassium dichromate, thus showing the presence of amyl alcohol, which undoubtedly owed its origin to the fact that crude 80 per cent. alcohol was often used at that time in the preparation; and during rectification it is possible for vapors of chloroform to carry over traces of fusel oil.

[9] *J. Pharm. Chim.*, **4**, 259.

[10] This test was as follows: A piece of filter paper saturated with the chloroform should dry completely, and the odor remain pleasant to the end the contrary was said to indicate the presence of amyl alcohol.

[11] *J. Pharm. Chim.*, [4] **30**, 405.

fully conducted test for odor has been generally recognized, notwithstanding the fact that it sometimes happens that only a very impure chloroform will leave any unpleasant odor after evaporation and that occasionally the residue is of a pleasant odor.[1] The first condition is dependent upon the nature of the test, especially its lack of delicacy; but even if the residue possesses a pleasant odor, if this is foreign, the chloroform must be contaminated.

Tilden[2] recommended the hand evaporation test for odor, while Regnault[3] recommended the method which has come into general use—evaporation on paper. It is generally stated that "pyrogenous oils," etc., may be detected in anaesthetic chloroform by allowing a definite volume to evaporate from a large piece of filter paper placed on a warm plate, when no foreign odor should be perceptible. The *British Pharmacopoeia* employs 20 cc. for this test; the *Pharmacopoeia of the United States* 10 cc.; while the German Pharmacopoeia specifies no particular amount. The *British Pharmacopoeia* requires that no odor should be perceptible at any stage of the evaporation;[4] the *Pharmacopoeia of the United States* that an odor should not be perceptible at the later stages of the evaporation and that the paper should remain odorless;[5] and the German Pharmacopoeia that the paper retain no foreign odor after the evaporation of the chloroform. We have found that the anaesthetic chloroform now on the market rarely imparts an odor to filter paper, on evaporation, even when 50 cc. of the sample are tested, notwithstanding the fact that it frequently contains small amounts of contaminants productive of a foreign odor but unrecognizable by the tests in general use, owing to their lack of delicacy. Since a carefully conducted test for odor is essential, principally owing to the fact that such impurities affect the keeping qualities of chloroform *per se*, although they may not occur in such amounts as to interfere with its physiological action, it has been noted by several investigators that it is necessary to employ a test which will render the presence of these evident.

Schwarz and Will[6] proposed a very rigorous test for the presence of amyl compounds in chloroform. 300 g. are distilled on a water bath until about 2 cc. remain in the flask; on the addition of concentrated sulphuric acid to this residue, no darkening should occur nor should an odor of amyl compounds be developed.[7] Brown[8] proposed that the sample of chloroform under examination be carefully fractionated until a residue of 15 per cent. remains, then that this be slowly evaporated at from 80° to 90°; bad or foreign odors are looked for during and at the conclusion of the evaporation, and the dry non-volatile residue is weighed. Later[1] Brown specified this test as follows: When distilled, the first 10 per cent. fraction and the 15 per cent. residue should be free from color and foreign odor, and the weight of the 15 per cent. residue after evaporation at 32° C. until constant, should not exceed 1 in 900,000 parts by weight. Langgaard[2] recommended a test for odor which is similar to that of Schwarz and Will. According to this method, the chloroform is vaporized in a long-necked flask on a water bath, down to a residue of 2 to 3 cc., care being taken that the chloroform does not boil; this residue is then placed on a watch-glass and allowed to evaporate slowly. The residue should be odorless and should show no reaction with formalin-sulphuric acid.[3] Such a test shows the presence of impurities not made evident by the usual official tests. A modification of these fractional evaporation methods is to be found in the *Pharmacopoeia Nederlandica*,[4] however. In this pharmacopoeia it is stated that "chloroformum ad narcosin" shall conform to the following test: 50 cc. of the chloroform are distilled until about 2 cc. are left; the residue is then allowed to evaporate on filter paper. There should then result no odor of alcohol, fusel oil or pungent matters.

The authors find that when anaesthetic chloroform is fractionated in the usual way, any chlorinated decomposition products, fusel oil, or higher alcohols present are concentrated in the residue remaining above 64°; and that when no indications of the presence of such compounds were had by the test prescribed by the United States Pharmacopoeia, the residue resulting from the distillation of 100 cc. gave a marked response. Anaesthetic chloroform should conform to the following requirement:—

100 cc. of anaesthetic chloroform are slowly evaporated over a water bath until about 10 cc. remain in the flask. This residuum should be colorless and possess no foreign odor; and when it is allowed to evaporate on filter paper, there should result no odor of fusel oil, empyreumatic matter, or other substances than chloroform and ethyl alcohol, as the last portions disappear. If a decided odor is imparted to the filter paper, after the evaporation of the residue or if any foreign odor is observed during the course of evaporation, the chloroform should be rejected for anaesthetic purposes, but for further information may be tested for such impurities as fusel oil, chlorinated derivatives of alcohol, acetone, or the higher alcohols, extractive matter, etc. The nature of the impurity in this case is often indicated by the odor itself. This test is indeed comparatively stringent and its adoption would necessitate rigid chemical

[1] *Pharm. J.*, [2] **6**, 576.
[2] *Ibid.*, [3] **1**, 623.
[3] *J. Pharm. Chim.*, [4] **29**, 402.
[4] The Ph. Brit. Committee of Reference in Pharmacy recommend that the test for odor be made with 10 cc. (*Chem. and Drug.*, **69**, 863). White *Pharm. J.*, [4] **25**, 540) has suggested that the test for odor be made as follows: 10 mils. are poured on a 10 cm. filter paper; no foreign odor should become perceptible as the last portion disappears, and the filter paper should be left odorless.
[5] "If 10 cc. of chlotoform be poured upon a piece of clean, odorless filter paper laid flat upon a warmed plate, and the plate be rocked from side to side until the liquid is all evaporated, no foreign odor should become perceptible as the last portions disappear from the paper, and the paper should be left odorless" (The *Pharmacopoeia of the United States*, **1905**, 99).
[6] *Pharm. Ztg.*, **1888**, 551.
[7] See the *Test with Sulphuric Acid*
[8] *Pharm J.*, [3] **23**, 229.

[1] *Pharm. J.*, [3] **25**, 865.
[2] *Therap. Monatsh.*, May, 1902; see also *Apoth. Ztg.*, **17**, 341; *Pharm. Centralh.*, **43**, 543; *J. Pharm. Chim.*, [6] **16**, 305.
See *Tests for Residue* and the *Test with Sulphuric Acid*
[4] **1905**, p. 90.

control on the part of the manufacturers; but *pure* anaesthetic chloroform may be, and is being, made on a commercial scale.

2. RESIDUE.

Until quite recently anaesthetic chloroform usually contained fixed matter, as shown by the residue remaining after evaporation at 100° C. Such contamination was generally due to carelessness in manufacture[1] and storage.[2]

At the present time, although sufficient care is generally exercised in manufacture and purification to prevent extraction, yet anaesthetic chloroform sometimes contains extractive matter, especially when it has been stored in unprotected cork-stoppered containers. For example, we found that anaesthetic chloroform sold as chemically pure might contain as much as 0.0011 per cent., by weight, of extractive matter non-volatile at 100° C., while in the case of commercial chloroform the residue often amounted to 0.0047 per cent. by weight. It is almost needless to point out that although such matter would not interfere with the applications of chloroform of either grade, for its special purposes, except when employed in certain analytical work, its presence affects the keeping properties of chloroform, and moreover is unnecessary when proper care is exercised in manufacture and storage.

In the opinion of the authors, when 100 cc. of anaesthetic chloroform are allowed to evaporate in a platinum dish at 100° C., there should be left no weighable residue. In every case this should be determined gravimetrically and not by vision.[3]

3 (*a*) THE TEST WITH SULPHURIC ACID.

Pure chloroform is not appreciably soluble in concentrated sulphuric acid; but when anaesthetic chloroform is agitated with that reagent, the alcohol present is removed[4] and decomposition occurs on exposure to air. It is therefore important that any treatment with sulphuric acid be not unduly prolonged; for even if the conditions are such that the sulphuric acid does not act directly upon the chloroform,[1] it must be borne in mind that its presence accelerates the oxidation of pure chloroform.[2] As has been indicated, it was early ascertained that treatment with concentrated sulphuric acid was an efficient means for the purification of crude chloroform; it therefore followed that the reagent would serve as an indication of purity—that no coloration should be imparted to the acid when it was shaken with chloroform. In fact, the test has been pharmaceutically recognized since 1847,[4] and has been generally regarded as both fair and useful, although it has been variously stated and modified to suit local conditions of production and trade requirements.

Gregory[5] considered that chloroform that was to be employed in surgical operations should not afford any yellow or brown coloration when it was shaken with sulphuric acid; and Vulpius,[6] in the course of a study of anaesthetic chloroform, examined six different grades of chloroform, finding that that which answered most satisfactorily in surgical operations was ordinary chloroform which, however, withstood the test with sulphuric acid. In dissidence with these findings is the view of Abraham,[7] who expressed doubt as to whether the substance which darkened sulphuric acid was always that which produced the unpleasant effects sometimes attributed to chloroform, as claimed by Gregory;[8] Abraham inferred that the substance which blackened or otherwise colored sulphuric acid was not always the same,[9] in agreement with which we have the divergent views which have been expressed as to the source of the coloration.

Morson[10] considered it probable that "heavy muriatic ether" caused the darkening of sulphuric acid; Hager[11] gave the test for the presence of acetone, aldehyde, and ethyl ether; Regnault[12] stated that a coloration indicated the presence of "alcoholic chlorides;"[13] a response has been considered indicative of preparation from methyl alcohol;[14] Schwanert[15] gave the test with an equal volume of sulphuric acid for hydrocarbons; Traub[16] found that chloroform prepared

[1] From the use of impure chemicals. Scholvien (*Apoth. Ztg.*, **1887**, 14; *Z. anal. Chem.*, **26**, Part 3) found that with many samples of chloroform then on the market, silver nitrate produced, after a short time, a dark brown turbidity, which could be removed by nitric acid and which did not form at all if the solution did contain a little nitric acid from the first; this he traced to the presence of arsenic in the chloroform examined. As a test for this impurity, he suggested that the chloroform be stirred with a dilute potassium hydroxide solution, evaporated, and the residue tested by Marsh's or Bettendorf's method. When such chloroform was distilled, Scholvien found that the arsenic remained in the residue, none passing into the distillate. The presence of arsenic in chloroform could have originated from the use of an arsenical bleaching powder, which, with the alcohol, would form, it is likely, arsenical organic compounds which would first distil over with the chloroform, yet not be capable of distillation from the chloroform itself; but more likely to the use of impure sulphuric acid in purification. Although other experimenters also reported having found traces of arsenic in samples of commercial chloroform, its presence is now improbable, even in commercial chloroform. Mentin (*Pharm. J.*, [3] **19**, 991) reported that 49 cc. of Saxon "Chloroformum Purissimum" gave a residue weighing 0.0006 g., possessing an odor of rancid butter; and that another chloroform manufactured from chloral yielded a residue weighing 0.0011 g., possessing a sweet, aromatic odor.

[2] When chloroform is supplied in tin containers, it sometimes happens that a small amount of zinc chloride, used as a flux in soldering "tins" by manufacturers, is introduced accidentally into the chloroform. Fixed matter is more generally introduced through the use of cork stoppers, however.

[3] White (*Pharm. J.*, [4] **25**, 540) proposed that when 10 mils of chloroform are allowed to evaporate in a clean glass beaker or dish, which is afterwards heated on a water bath, there should be left no *visible* residue.

According to Kessler (*J. Pharm. Chim.*, [3] **13**, 162), chloroform containing alcohol diminishes in volume on agitation with sulphuric acid.

[1] On the action of sulphuric anhydride on chloroform, see Armstrong *Proc. Roy. Soc.*, **18**, 502; *J. prakt. Chem.*, [2] **1**, 244.

[2] See *Decomposition*. Brown (*Pharm. J.*, [2] **6**, 576) pointed out that a sample of chloroform tested with sulphuric acid should not be returned to the stock, since chloroform twice treated with sulphuric acid is likely to decompose. See *Alcohol*.

[3] Under *Purification*.

[4] Cf. *Codex Medicamentarius Hamburgensis*, 1847, wherein it is specified that chloroform should not color concentrated sulphuric acid.

[5] *Proc. Roy. Soc. Edub.*, **1850**, 391.

[6] *Archiv. Pharm.*, [3] **13**, 37; **25**, 998.

[7] *Pharm. J.*, **10**, 25.

[8] *Chamber's J.*, May 4, 1850.

[9] Abraham stated that pure chloroform left no odor when allowed to evaporate from the hand or cloth, and that impure chloroform afforded an odor which was generally proportional to its effect in coloring the acid. He also reported that the specimen which colored sulphuric acid considerably left, if any, the least odor.

[10] *Pharm. J.*, **8**, 280.

[11] *Kommentar*, **1865**, p. 443.

[12] *J. Pharm. Chim.*, [4] **29**, 402.

[13] Brown (*Pharm. J.*, [3] **23**, 229) suggested that the extent to which sulphuric acid decomposed such impurities be determined.

[14] Cf. *Archiv. Pharm.*, December, 1874.

[15] *Hülfsbuch zur Ausführung Chemischer Arbeiten*, **1891**, p. 169.

[16] *Z. angew. Chem.*, **1892**, 192. Traub reported that sometimes an odor of peppermint was developed when the sulphuric acid test was applied to crude chloroform (*Pharm. Centralh.*, **33**, 245).

from alcohol by means of chloride of lime contained ethylidene chloride and "other impurities" which gave colored products with sulphuric acid;[1] Gay[2] stated that when the sulphuric acid became brown, the presence of chloro-derivatives of ethyl acohol or of the higher homologues was indicated; Schacht and Biltz[3] reported that when chloroform which was pure and free from alcohol, and which did not color sulphuric acid, was left to undergo decomposition, and the sulphuric acid after that became brown, this coloration was due to ethyl chloride;[4] others have employed the test to prove the absence of ethyl chloride and other ethane chlorides,[5] amyl and isobutyl alcohols,[6] amyl compounds,[7] or empyreumatic oily matter;[8] the test has been employed to show the presence of excessive amounts of alcohol or water;[9] and finally it has been stated that "pure chloroform" floats on concentrated sulphuric acid with a contact-surface convex downwards, but if "impure" gives a plane contact-surface.[10]

It has been universally conceded, however, that anaesthetic chloroform should not afford a coloration with sulphuric acid, notwithstanding the fact that the cause of the coloration appears to be variable and consequently has not been determined. As to just how the test should be performed, especially the proportion of reagent to use and the proper time limit, has been the subject of much discussion and even now totally diverse opinions are held—a condition attributable, in the main, to the demand of the trade for pure anaesthetic chloroform at a minimum cost, and the position taken by the manufacturers and their chemists that, on the other hand, if the requirements are rigorous, the price must be proportionally increased, to which the trade is not ready to accede, except, apparently, in Germany, France, Russia, Holland, and Belgium.

Brown[11] suggested that the quantity of sulphuric acid used be fixed at 10 per cent. and that it be shaken with the chloroform continuously for 20 minutes, after which the acid should remain colorless or nearly so;[12] it has been stated that "good and genuine" chloroform should remain colorless when mixed with an equal volume of concentrated sulphuric acid, without specifying a time-limit;[13] Gay[14] directed that 10 cc. be shaken violently with an equal volume of sulphuric acid and that the mixture should remain colorless even for an hour; Vulpius[1] considered that no perceptible yellow color should result within one day; Schwarz and Will[2] proposed that 40 g. of the chloroform be shaken with 30 g. of concentrated sulphuric acid in a glass-stoppered bottle, previously rinsed with sulphuric acid, and that the acid should not darken within 48 hours; and Traub[3] stated that a mixture of equal volumes of chloroform and sulphuric acid, when repeatedly shaken in the dark, should possess no discoloration after six to eight days.[4] From these variable recommendations it can readily be understood why important differences exist in the test as prescribed by various pharmacopoeias.

According to the *British Pharmacopoeia*, chloroform, when shaken with one-tenth its volume of sulphuric acid for 20 minutes, and then set aside for 15 minutes, should acquire practically no color in either the chloroformic or sulphuric acid layer and both should be quite transparent.[5] The Pharmacopoeias of Switzerland and Belgium specify a more rigorous test, namely: 15 cc. of acid are shaken with 20 cc. of chloroform in a stoppered glass cylinder of 3 cm. diameter previously rinsed out with sulphuric acid; the acid should not become colored within one hour. A similar test is given in the Pharmacopoeia of Japan. In Germany, it is now required that "narkose chloroform" give no color to sulphuric acid even after 48 hours, when 20 cc. of the sample are agitated with 15 cc. of acid. Formerly the time-limit was one hour,[6] but at present the test for this period of contact is restricted to chloroform other than that intended for anaesthesia.[7] According to the Pharmacopoeias of France, Sweden, Austria, Hungary and Spain, an equal volume of sulphuric acid is used; that of France states that no coloration should result even at the end of several hours, while the Pharmacopoeias of Austria and Hungary place a time-limit of one hour. The Pharmacopoeia of Denmark specifies that 20 g. of chloroform and 25 g. of acid be employed, and places the time-limit at one hour; the Norwegian requirement is similar; the Pharmacopoeias of Italy and Holland require that the test extend for 24 hours; while the Pharmacopoeia of Russia merely states "some time."

The test as given in the *Pharmacopoeia of the United States*[8] for "impurities decomposable by sulphuric

[1] Moreover, Traub found that by treating chloroform with sulphuric acid and other reagents, a chloroform might be obtained which in all respects was equal to Chloroform Pictet.

[2] *J. Pharm. Chim.*, **4**, 259.

[3] *Pharm. Centralh.*, **33**, 269.

[4] Dott (*Pharm. J.*, [3] **22**, 1080) maintained that ethyl chloride and ethyl alcohol gave no appreciable coloration with sulphuric acid. He stated that it is easy to arrive at false conclusions from the sulphuric acid test, since chloroform containing a mere trace of linseed oil derived from the jetting will give a decided reaction.

[5] E. Schmidt, *Z. angew. Chem.*, **23**, 1547.

[6] Cf. Schacht, *Archiv. Pharm.*, [3] **27**, 865.

[7] E. Schmidt, *Loc. cit.*

[8] *United States Dispensatory*, 18th Ed., p. 380.

[9] *Ibid.*

[10] Allen's *Commercial Organic Analysis*, **1**, 236. According to Soueiran (*Ann. chim. phys.*, [2] **48**, 131), pure chloroform sinks in a mixture of equal parts of sulphuric acid and water.

[11] *Pharm. J.*, [3] **23**, 229; **25**, 865.

[12] Brown stated that on diluting with 3 volumes of water, the mixture should remain colorless and clear, and should give off only a slight foreign odor.

[13] *Polyt. Notizblatt*, **1875**, 16.

[14] *J. Pharm. Chim.*, **4**, 259.

[1] *Archiv. Pharm.*, [3] **25**, 998.

[2] *Pharm. Ztg.*, **1888**, 551.

[3] *Z. angew. Chem.*, **1892**, 192.

[4] Traub recommended that the chloroform and acid be then separated, and that the acid be next diluted with 5 parts of water, to which 1 cc. of *N*/10 silver nitrate is added; no alteration should result, although, according to Traub, only a "very pure" product will stand this test.

[5] 2 cc. of the sulphuric acid obtained on shaking with chloroform, as described, is then diluted with 2½ times its volume of water, after which it should remain clear, almost colorless, and should possess a pleasant odor. It is required that the liquid should still retain its transparency and freedom from color, even when further diluted with 10 cc. of water and stirred with a glass rod, and that the transparency should not be more than slightly diminished on the addition of 4 drops of silver nitrate solution.

[6] Such a test is given by Krauch (*Testing of Chemical Reagents*) **1902**, p. 78).

[7] See *Deutsches Arzneibuch*, **1910**, 118.

[8] **1905**, 99. For reference to the other Pharmacopoeias mentioned above, see *Specific Gravity* tables.

acid" hardly bears comparison with the above in point of delicacy. It is required that "if 40 cc. of chloroform be shaken with 4 cc. of colorless, concentrated sulphuric acid in a 50 cc. glass-stoppered cylinder during 20 minutes, and the liquids be then allowed to separate completely, so that both are transparent, the chloroform should remain colorless, and the acid should appear colorless, or very nearly colorless, when seen in a stratum of not less than 15 mm. in thickness." This test has been required since 1893,[1] and the test as specified until the seventh revision of the Pharmacopoeia was considerably more stringent, if less specific.[2]

3 (*b*) THE TEST WITH FORMALIN-SULPHURIC ACID.

Langgaard[3] recommended a test, by means of which the slightest traces of amyl compounds are said to be detectable. Concentrated sulphuric acid and chloroform are mixed in the proportion in which the German Pharmacopoeia indicates when testing for amyl compounds, etc., in a glass-stoppered vial which has been previously rinsed with sulphuric acid, and, after the addition of 3 or 4 drops of formalin (35–40 per cent. solution of formaldehyde), the mixture is well shaken; no coloration should result. The *Deutsches Arzneibuch*[4] requires that 20 cc. of "narkose chloroform" shall afford no coloration with 15 cc. of sulphuric acid and 4 drops of formaldehyde solution, but gives the test for the presence of organic decomposition products.

3 (*c*) DISCUSSION OF 3 (*a*) AND 3 (*b*).

A. Sulphuric acid is well-known as a reagent for the presence of furfural in amyl and methyl alcohols; of fusel oil, "empyreumatic oils," or "non-volatile carbonizable organic impurities" in ethyl alcohol and ethyl ether; and of "readily carbonizable organic impurities" in acetic ether, glycerin, and salicylic, lactic and benzoic acids. The authors have pointed out[5] that in the case of ethyl ether, the color reaction may be caused in general by the following:

1. Furfural with isobutyl alcohol, tertiary butyl alcohol, tertiary amyl alcohol, acetaldehyde, acetal, aceto-acetic ether, acetone, methyl alcohol, or isopropyl alcohol, or mixtures of these.[6]
2. Fusel oil.
3. Extractive matter from cork, etc.

We can now report, after examining a number of samples of 24 different varieties of anaesthetic chloroform, that when a properly stored sample of chloroform gives a response when the test with sulphuric acid is applied, this is usually due to the presence of one or more of the above contaminants.

We have found that anaesthetic chloroform which afforded only a faint coloration with sulphuric acid originally, being apparently free from fusel oil, extractive matter, etc., gives a marked reaction on treatment with oxygen, on continued agitation in the presence of air, after lengthy exposure to air and light, and on long standing in anactinic glass with the customary amount of air present. The last condition is of particular interest, since anaesthetic chloroform is frequently one year old, or more, when it reaches the consumers, and for this reason the matter was investigated in the laboratories of one of the large producers of chloroform. This concern reports as follows concerning the experiments made and conclusions arrived at:—

Three varieties of chloroform were used, these being obtained from independent manufacturers of known reputation. They were exposed in two ways: 1st, in amber bottles exposed to only indirect light on the dark side of a room; and 2nd, in white glass bottles exposed to bright, diffused light near a window. The experiments covered one year, from January, 1908, to January, 1909. All samples were tested by the sulphuric acid test of the U. S. P. on fresh samples before starting. In every case the acid showed some color in a 15 mm. layer. This color was matched in every case by a one-thousandth normal iodine solution, the latter being diluted until it exhibited the same color as the acid. In the beginning, the acid in all three samples showed the same degree of color, namely, that corresponding to 0.3 cc. of $N/1000$th iodine solution diluted to 3 cc. After one year's keeping in brown bottles, the color had become more than three times as deep as at the beginning, since now 1 cc. of $N/1000$th iodine solution diluted to 3 cc. was required to match this color. The samples kept in the white bottles showed in some cases the same amount of change in color; others showed a *greater* change, the maximum being five times as deep as the color at starting. All bottles were closed with ground glass stoppers.

In another series of experiments, the samples of chloroform were sealed in white glass test tubes and submitted, as before, to the sulphuric acid test before and after exposure for one year to bright light under a skylight. In this case the color deepened to a tint from *four to thirteen times darker* than at starting.

"It appears, therefore, that the best chloroform to be obtained imparts a very decided color to sulphuric acid when shaken with it after keeping in brown glass

[1] See *Pharmacopoeia of the United States*, 7th revision, p. 88.

[2] The Pharmacopoeia of 1851 (p. 76) required that with an equal volume of sulphuric acid, chloroform should not assume a reddish brown color nor should the acid become discolored; the Pharmacopoeia of 1869 (p. 87) specified that the acid and chloroform should remain in contact 24 hours, at the end of which time no color should be imparted to either liquid or but a faint yellowish tinge to the acid; in the fifth revision (1873, p. 78) the last-mentioned test was retained; and in the sixth revision (1882) it was required that on shaking 10 cc. of chloroform with 5 cc. of sulphuric acid, no color should be imparted to either liquid after 24 hours.

[3] *Therap. Monatsh.*, May, 1902; on the employment of the reagent of Marquis for testing anaesthetic chloroform, see also Stadlmayr, *Z. angew. Chem.*, **23**, 1548; Linke, *Apoth. Ztg.*, **25**, 189, 285, 426.

[4] **1910**, p. 118; see in this connection, Braun, *Apoth. Ztg.*, **26**, 166, who favors a time limit of 48 hours for the sulphuric acid test, and considers that the formalin-sulphuric acid test is of value only when used upon chloroform before the addition of the alcohol necessary to prevent decomposition. It will be shown later that *pure* anaesthetic chloroform gives no reaction with formalin-sulphuric acid.

[5] THIS JOURNAL, **3**, 306.

[6] It may be mentioned here that the authors have had occasion to examine various samples of so-called higher alcohols and their derivatives, sold as chemically pure. Samples of normal butyl alcohol and iso-amyl ether invariably contained furfural; samples of active amyl, iso-amyl, iso-propyl alcohols and propyl aldehyde gave marked reactions with sulphuric acid, but only very faint reactions for furfural; while samples of propyl, iso-butyl, tertiary butyl and methyl alcohols gave a yellow color with sulphuric acid, but no reaction for furfural. All of the samples were properly stored, except that air was invariably present, and we can only attribute the results to oxidation products.

bottles shaded from bright light for one year, and at the end of that time decidedly fails to meet the pharmacopoeial requirement in this regard."

At the end of the series all the samples were submitted to the U. S. P. tests for chlorides and free chlorine. One sample in brown glass showed a faint opalescence under the chloride test and one sample of the same producer in white glass showed a very marked opalescence under the same test. All other samples gave no reaction for chlorides. None of them gave any color when submitted to the test with potassium iodide.

"It therefore appears that the samples of chloroform, after keeping under favorable conditions for one year, show no deterioration as measured by the formation of chlorides or free chlorine, while they nevertheless fail to meet the U. S. P. sulphuric acid test."

It may be mentioned that these samples were examined not merely at the end of the year, but at the end of each quarter, which, of course, necessitated the opening of the containers. The change was *progressive*, although in only one case was there any alteration between the third and fourth quarter.

"We cannot help thinking that these results at least suggest the desirability of considering a modification of the sulphuric acid test for chloroform, possibly in the direction of defining more closely what is meant by 'very nearly colorless.' The use of a standard iodine solution affords a convenient method for defining this color."

The results obtained by the authors on samples of anaesthetic chloroform agree with those given above in these respects:

1. Fresh samples of American anaesthetic chloroform very frequently afford a slight coloration with sulphuric acid.[1]

2. Samples exposed to air in colorless glass bottles are usually oxidized to a greater degree than those stored in bottles of anactinic glass.

3. After prolonged exposure to air and light, a reaction for chlorides is rarely obtained. In a few of the cases where the presence of chlorides was indicated, we found that the oxidation of the alcohol present had reached a maximum and decomposition of the chloroform itself had consequently resulted; but this represents the extreme condition, and only occurred when the anaesthetic chloroform originally contained an amount of alcohol less than 0.25 per cent. and had been very carelessly stored. In most of the cases, the reaction with silver nitrate solution was not due to the presence of chlorides, but to acetaldehyde, etc.

4. The oxidation, as we prefer to term the alteration which undoubtedly occurs, is progressive when constant conditions are maintained, and the presence of air is necessary. It will therefore be seen that repeated opening of chloroform containers favors decomposition; and as more air is introduced after each sampling, the conditions for oxidation are progressively rendered more favorable.

We have previously emphasized the importance of having anaesthetic chloroform free from the so-called "organic impurities," which, as a rule, afford a coloration with sulphuric acid, since these accelerate the oxidation of anaesthetic chloroform. Here we may mention that samples of anaesthetic chloroform which showed absolutely no response to sulphuric acid originally, became only very slightly oxidized after seven months' storage in bottles of anactinic glass, and exposed to diffused daylight, and afforded no reaction with sulphuric acid after this time. We are therefore of the opinion that if *pure* anaesthetic chloroform is properly stored, it may be kept in an unaltered condition for at least seven months, and that it is unnecessary to modify the test with sulphuric acid.

Six samples of anaesthetic chloroform, which had been stored in brown glass bottles for twenty-one months in the factory of a well known chemical manufacturer, were given to the authors for examination, and every sample was found to comply in full with the tests prescribed by the *Pharmacopoeia of the United States*. None contained "impurities decomposable by sulphuric acid," although the presence of higher alcohols, evidently, was detected by the formalin-sulphuric acid test.

In order to ascertain the secondary causes of the reaction with sulphuric acid—that is, to determine what compound or compounds are formed in the oxidation of anaesthetic chloroform which may produce the coloration—the deportment of the following possible oxidation products and chlorinated derivatives was determined in chloroformic solution: acetaldehyde, acetic acid, chloracetic acid, ethyl acetate, ethyl chloride, "ethyl chloride polychlorated" (a mixture of tri-, tetra-, and pentachlorethane), ethylidene chloride, ethylene chloride, carbon dichloride, carbon trichloride, and chloral hydrate. Of these, only "ethyl chloride polychlorated" afforded a decided reaction, although we were inclined to attribute it to the presence of an impurity. Since acetal, which results in the imperfect oxidation of ethyl alcohol, is decomposed by sulphuric acid, the conduct of this compound in chloroform solution towards sulphuric acid was also investigated. It was found that the presence of 1 part of acetal in 2000 of chloroform gave a marked reaction with sulphuric acid,[1] but that 1 part in 3000 afforded only a very faint coloration. We concluded that acetal alone could not cause the reaction, since the coloration afforded by the presence of small amounts is not sufficiently intense and traces gave no reaction; but acetal is one of the possible products of the oxidation of anaesthetic chloroform, and the reaction may be attributed in some cases to its formation.

Another probable contaminant of anaesthetic chloroform is furfural, with which acetal and acetaldehyde give a coloration to sulphuric acid, although "metafurfural" alone gives the reaction. The presence of furfural in anaesthetic chloroform is likely to result

[1] One large firm of manufacturing chemists state, in fact, that they have never examined a sample of chloroform that would not become colored to some extent when shaken with sulphuric acid under the conditions of the U. S. P. test."

[1] The acetal used was furfural free.

either from the use of impure alcohol, in which case a coloration would be had with sulphuric acid just as soon as the alcohol became oxidized; or from the oxidation of anaesthetic chloroform,[1] although, in our opinion, this is less likely, since we have been unable to detect its presence in samples of anaesthetic chloroform exposed to air and light for seven months, even when saturated with water and hydrogen dioxide solution, or in samples one year old customarily stored. In every case where we found furfural in samples of anaesthetic chloroform, higher alcohols were also present, and in these cases its presence was to be attributed to the occurrence of fusel oil in alcohol used in the production; such chloroform, of course, gave a marked reaction with sulphuric acid.

B. In order to determine the value of the test with formalin-sulphuric acid, 20 cc. of various anaesthetic chloroforms were thoroughly shaken with 15 cc. of concentrated sulphuric acid and 4 drops of formalin,[2] and then any coloration was observed. Only those American products were used which gave a negative or very faint reaction with sulphuric acid alone; these were then compared with anaesthetic chloroforms of German manufacture.

The results may be thus tabulated:

AMERICAN PRODUCTS.

Sample.	Results.
1. "Chloroform U. S. P." This sample contained 0.7 cc. absolute alcohol in 100 cc., and conformed to all the U. S. P. tests.	Yellowish brown color at once; brown color after standing 5 minutes.
2. "Purified chloroform." This sample contained 0.97 cc. absolute alcohol in 100 cc., and was of full U. S. P. grade.	Very faint color after 1 minute; faint yellow color after 5 minutes.
3. "Chloroform Purified." This sample contained 0.5 cc. absolute alcohol in 100 cc., and conformed with all the requirements of the U. S. P., except that it gave a faint coloration with sulphuric acid (unprotected cork stopper). This chloroform was made from acetone.	Faint yellow color after 1 minute; faint brown color after 5 minutes.
4. "Purified Chloroform." This sample contained 0.74 cc. absolute alcohol in 100 cc., and answered all the U. S. P. tests. This chloroform was made from carbon tetrachloride.	Very faint after 1 minute; faint yellow color after 5 minutes.
5. A sample of anaesthetic chloroform 21 months old, but of full U. S. P. quality.	Reddish yellow color after 1 minute; marked brown color after 5 minutes.
6. "Chloroform Pure." A sample which contained 0.56 cc. absolute alcohol in 100 cc., and which was of full U. S. P. standard.	No coloration after 5 minutes.
7. "Purified Chloroform." A sample of chloroform made from acetone, containing 0.84 cc. of absolute alcohol in 100 cc. and which passed all the U. S. P. tests, except that it gave a faint color with sulphuric acid.	A very faint yellow color after 5 minutes.

[1] From ethyl alcohol through chlor-acetal (Lieben, *Ann.*, **104**, 114; **146**, 193.

[2] The formalin used dissolved in sulphuric acid to form a perfectly transparent, colorless solution.

GERMAN PRODUCTS [1]

Sample.	Results.
1. "Chloroform Pictet," density 1.49 at 15.15°.	No coloration after 5 minutes.
2. "Salicylid-Chloroform," density 1.497 at 15/15°.	No coloration after 5 minutes.
3. "Chloroform chem. rein.," density 1.488 at 15/15°.	No color after 5 minutes.
4. "Chloroform chem. rein.," density 1.4887 at 15/15°.	Exceedingly faint color after 5 minutes.
5. "Chloroformium Purissimum," density 1.4888 at 15/15°.	Very faint after 1 minute, yellow color after 5 minutes.
6. "Chloroform chem. rein.," density 1.487 at 15/15°.	No coloration after 5 minutes.
7. "Chloroform Ph. G. IV.," density 1.489 at 15/15°.	No color after 5 minutes.

These results show that the test with formalin-sulphuric acid is indeed sensitive and that it will serve to detect impurities not made evident by sulphuric acid alone. We found that pure chloroform as well as *pure* anaesthetic chloroform gave no response, when 100 cc. were allowed to evaporate until but 10 cc. remained, and this residue was then tested with formalin-sulphuric acid.

Among the substances detectable by means of formalin-sulphuric acid, are: morphine (Marquis); morphine derivatives, such as codeine, heroine, peronine, and dionine (Kobert); and Linke showed that many alkaloids, phenol, salicylic acid, resorcin, phloroglucin, benzol, toluol, xylol, and other organic compounds, give color reactions. Casein, milk-whey, etc., give a blue color with the reagent. We have observed that samples of ethylene chloride, carbon dichloride, chloracetic acid, ethyl acetate and chloral hydrate, supposedly pure and which afforded no coloration with sulphuric acid alone, gave a yellow color with formalin-sulphuric acid. In fact, it may be said that the reagent gives no distinctive reactions—it cannot be employed for purposes of identification; but we have found that *pure* anaesthetic chloroform gives no coloration with the reagent, and since anaesthetic chloroform should be pure, it is of no direct importance just what the contamination is. We have found that it is generally one or more of the higher alcohols, however, and that the greater sensitiveness of the reagent over sulphuric acid alone is due to the fact that a reaction is had in the absence of furfural—that is, when amyl, propyl or butyl alcohol is present in chloroform, the presence of furfural is unnecessary to obtain a reaction.

Samples of purified isopropyl, propyl, isoamyl, active amyl, tertiary amyl and isobutyl alcohols, free from detectable amounts of furfural, and which gave but a pale yellow coloration with sulphuric acid, afforded a red-brown color with formalin-sulphuric acid; in fact, the deportment was strikingly similar to the conduct of such compounds towards sulphuric acid when furfural is present, and showed the presence of furfural is not essential for a positive response.[2]

[1] All of the above anaesthetic chloroforms of German manufacture were of full Ph. G. IV. quality. It should be remembered, however, that the test with formalin-sulphuric acid was not specified until the 5th revision of the *Arzneibuch*. The comparison with the American chloroforms is thus on a more relative basis.

[2] It may be pointed out in this connection that the test with aniline-acetic acid is not characteristic of furfural, as is generally supposed, since formaldehyde also gives the reaction.

In order to determine the delicacy of the reagent as a test for the presence of higher alcohols in anaesthetic chloroform, the following comparative experiments were made, the observations being recorded immediately after mixing:

Chloroform, 20 cc.	Sulphuric acid, 15 cc.	Result on adding 4 drops of formalin.
Isobutyl alcohol, 1 : 6000	Faint coloration	Yellowish brown color.
Propyl alcohol, 1 6000	Faint color	Yellowish brown color; marked after 5 minutes.
Isobutyl alcohol, 1 : 12,000	Very faint color	Dark yellow.
Propyl alcohol, 1 : 12,000	Exceedingly faint color	Yellow color; brownish yellow after 5 minutes.
Isobutyl alcohol, 1 : 18,000	Negative	Yellow color which became more marked on standing.
Propyl alcohol, 1 18,000	Negative	Yellow color.
Isobutyl alcohol, 1 : 54,000		Yellow color.
Propyl alcohol, 1 . 54,000		Yellow color, easily discernible after 5 minutes.

We have found that even the presence of 1 part of isobutyl alcohol in 600,000 of anaesthetic chloroform may be detected by means of the formalin-sulphuric acid test, and therefore conclude that this test is indicative of the mere presence of higher alcohols in chloroform. A sample of anaesthetic chloroform complying with the test as prescribed by the *Deutsches Arzneibuch* is assuredly free from such contamination, and the indication is that it has been thoroughly purified, that pure alcohol is present, and that there is no contamination with impurities decomposable by sulphuric acid whatsoever—that is, the chloroform has been properly prepared and stored. Generally, when higher alcohols are present in anaesthetic chloroform, furfural is also present, and therefore the test with sulphuric acid alone is sufficient to show the presence of likely impurities in any probable amounts; but the formalin-sulphuric acid test is much more intense in such cases, and is consequently more rapid and delicate. This is shown in the above experiments, and it is only necessary to mention, in conclusion, that when sulphuric acid alone is used, often the time necessary for the reaction, if any at all is obtained, is four or five, and sometimes even twelve hours, with a sample of anaesthetic chloroform which affords a decided coloration with formalin-sulphuric acid in five minutes as a maximum.

C. It has been stated[1] that "salicylous acid" and concentrated sulphuric acid afford colorations with amyl and other higher alcohols; but owing to the difficulty in obtaining salicylous acid (C_6H_4.OH.COH) which affords no intense red coloration with sulphuric acid alone, this test is not to be recommended for the detection of such compounds in chloroform. It was the authors' original intention to employ pure furfural and sulphuric acid as a test for the presence of higher alcohols in chloroform; but this was rejected, owing to the difficulty of obtaining furfural which affords no coloration with sulphuric acid itself, and also because of the satisfactory delicacy of the formalin-sulphuric acid test.

[1] *Chem. Ztg.*, **34**, 470.

D. Anaesthetic chloroform should comply with the following test:—

When 20 cc. of anaesthetic chloroform are mixed with 15 cc. of concentrated sulphuric acid in a glass-stoppered tube of 50 cc. capacity, which has been previously rinsed with concentrated sulphuric acid, no visible coloration should be imparted to the mixture after the addition of 0.4 cc. of a pure 40 per cent. formaldehyde solution, and then shaking throughout a period of 5 minutes.

Anaesthetic chloroform which conforms with this requirement, may, when properly stored, be kept for long periods of time without undergoing oxidation; and we have found that for the production of such chloroform it is not necessary to resort to the several special patented processes of purification in use by certain European firms.

(*To be continued in the July No.*)

SOME DATA ON THE MANUFACTURE OF SMOKING OPIUM AND ITS CHEMICAL COMPOSITION.[1]

By A. B. Adams and James M. Doran.

Received February 1, 1912.

Under the Federal laws in regard to the manufacture, sale and consumption of opium for smoking purposes, the Internal Revenue laboratory has had occasion during the last two years to do some work on smoking opium. Finding practically no literature on the subject, at least on the manufacture of opium for smoking purposes in the United States, it is thought that some of the information gathered on the subject as a result of the work might be of interest.

Briefly, smoking opium is an aqueous extract of gum opium evaporated to such a consistency that it may be smoked in an opium pipe; that is, the consistency of thick molasses. It has the characteristic odor of opium.

The Federal law of 1890 imposed a heavy Internal Revenue tax on the manufacture of opium for smoking purposes, and up to February, 1909, prepared smoking opium could be imported under heavy duties. In February, 1909, Congress passed a law prohibiting the importation of any opium for other than medicinal purposes, after April 1, 1909.

In the year 1908 there were imported into the United States 147,624 pounds of smoking opium. To supply this almost constant demand for smoking opium in the United States, there are two avenues open; first, to smuggle in smoking opium already prepared in China or other places outside of the United States, or, second, to illicitly manufacture the opium in the United States, thus evading the prohibitory customs laws and the Internal Revenue laws relating to its manufacture in this country. It is in connection with the prosecution of the illicit manufacturing of smoking opium in the United States that practically all of these data were obtained.

Opium is the exuded juice obtained by scarifying the partially ripe seed-capsule of the variety of the poppy, *papaver somniferum*. It is gathered in a partially

[1] Published by authority of the Commissioner of Internal Revenue. Read before the Division of Pharmaceutical Chemistry, American Chemical Society Washington Meeting, Dec., 1911.

dried gummy mass and packed together in one- to four-pound cakes, which are the crude gum opium cakes of commerce.

The black poppy is cultivated chiefly in Asia Minor. The gum obtained from it is high in content of morphine, making it especially valuable for pharmaceutical purposes.

The white poppy is cultivated in China, India, Persia and Egypt. The opium obtained from it is uniformly low in morphine.

The Chinese gum, likewise the Indian gum, is entirely consumed locally, chiefly in the manufacture of smoking opium.

Thorpe[1] states that the Chinese recognize four varieties of opium, namely:

1. Raw or crude opium (that is, the crude gum opium).

2. Prepared opium (or the finished product for smoking).

3. Dross or pipe cleanings (the ash remaining after smoking. This is known among Chinamen, at least in the United States, as Yen-Shi).

4. Opium dirt, or the exhausted marc after extraction of the gum opium.

The statement is also made by Thorpe under the authority of McCallum that the Chinese of Hong-Kong prepare smoking opium by extracting the gum opium with water and evaporating the clear extract to the consistency of treacle.

In this country, so far as known, practically the same process is followed; the gum opium, broken in small pieces, is extracted with boiling water in a suitable vessel. This extract is drawn off through a suitable strainer, usually cheese cloth, to separate the refuse matter, poppy leaves, crude fiber, etc. In some instances U. S. P. powdered opium has been used by placing it in cloth bags and boiling it in water. In either case the clear extract is evaporated down, or rather boiled down, to the consistency of thick molasses. It is then ready for use.

In this country there is added to the evaporating mass, in some cases, the water extract of the Yen-Shi, or pipe residue, and in other cases the Yen-Shi in toto. This practise is claimed by some to add flavor to the finished product, but as the use of Yen-Shi or Yen-Shi extract has not been detected in smoking opium of known Chinese manufacture, it is fair to assume that its use in this country is purely a matter of economy in the recovery of some of the unconsumed opium in the Yen-Shi, or possibly the familiar process of adulteration.

No record is shown of any importation of Chinese gum into the United States. All gum opium imported and used commercially in the United States is the product of Asia Minor, or Smyrna gum.

It is evident that we may assume that if any gum has been manufactured into smoking opium in the United States it was Smyrna gum; consequently the resulting prepared smoking opium should be of uniformly high morphine content.

[1] "Dictionary of Applied Chemistry," Vol. 3, p. 72. See also Hartwitch, "Die Menschlichen Genussmittel."

On the other hand, smoking opium prepared in China should be of a uniformly low morphine content, owing to its source.

Our analytical results showed this to be the case.

Chinese smoking opium is put up for the market in small bronze boxes about $3^1/_2 \times 4^1/_2 \times 1^1/_2$ inches. The box is usually about $^2/_3$ full, the net weight of the opium being 5 taels or $6^2/_3$ ounces. When these cans were regularly imported they were covered by a gummed customs strip stamp.

A can of customs tax-paid smoking opium with stamp intact is valued at about $95.00, due largely to the fact that the can may be refilled with but little chance of detection as long as the stamp holds together, the opium in the can being in a legal container. A can of smuggled opium is worth about $40.00.

A small quantity of smoking opium was prepared in the laboratory from Smyrna gum. The weight of the gum used was $5^1/_2$ ounces; the weight of the smoking gum obtained was $3^7/_8$ ounces. The best information seems to be that in the illicit manufacture of smoking opium in the United States the weight of the finished is from $^1/_2$ to $^2/_3$ that of the raw material used. At the price of crude gum opium in this country the manufacturing of smoking opium is very profitable, due to the high price that habitues of "smoking" will pay to obtain their "hop."

The old U. S. P. extract of opium is a product similar in every way to the smoking opium illicitly manufactured in the United States, and it is worth noting that considerable U. S. P. extract of opium, made by several large drug firms, has been found and has been known to have been used for smoking in many opium dens or so-called "hop joints."

Several samples of genuine Chinese smoking opium have been analyzed in this laboratory, some being samples smuggled into this country and others imported before April 1, 1909.

The following is a capitulation of the analyses in percentages:

	Smuggled 5 samples.			Regularly imported 13 samples.		
	Morphine.	Moisture.	Ash.	Morphine.	Moisture.	Ash.
Average	6.41	18.71	5.53	7.86	15.50	3.98
Maximum	7.40	21.55	6.17	9.59	19.48	6.96
Minimum	5.30	16.61	4.66	5.91	11.64	5.38

Of the many samples of smoking opium illicitly manufactured in the United States which were examined in the laboratory the five following are typical analyses:

	Morphine. Per cent.	Moisture. Per cent.	Ash. Per cent.
1	17.49	17.06	9.43
2	14.37	10.51	10.48
3	18.47	21.96	...
4	16.98	20.68	4.61
5	16.53	17.67	...

These samples were manufactured in Denver, New York City, Pittsburgh, Terre Haute, and Buffalo, respectively.

An aqueous extract of Yen-Shi was made in the laboratory and it was attempted to evaporate it down to the consistency of smoking opium. It became hard and brittle when the moisture content was about the

me as that of smoking opium. It is evident that tisfactory smoking opium cannot be made from en-Shi exclusively, due largely to the lack of the sinous and gummy matters that give to smoking ium its proper consistency.

The extract of Yen-Shi is uniformly high in ash, in e above-mentioned instance being 19.00 per cent. appears that the ash of opium is largely water luble, and a high ash content of a prepared smoking ium is a rather useful indication of the use of Yen-i extract.

Yen-Shi and Yen-Shi extract has a distinctive and culiar odor. The recognition of this odor in the ished product is a valuable indication of the use of en-Shi.

The process of smoking opium is substantially as llows:

A small mass of the material about the size of a pea taken up on a "dipper" or a small metal rod, known a Yen-Hook. This lump is dexterously rotated the flame of a small lamp, usually a peanut oil lamp, til the excessive moisture is driven off and the mass partly incinerated, or until the "pill is cooked."

It is then placed in the bowl of the opium pipe and ld just over the flame of the lamp, and the smoke om the "pill" inhaled. The preparations for smok-g occupy 10 to 15 minutes, the actual operation of ioking about 30 seconds.

No attempt is made in this paper to give an exhaus-ve analysis of smoking opium, which is the same in l essentials as gum opium and its products, on which ere is already a mass of literature.

Further work is being done in this laboratory on e composition of Yen-Shi and Yen-Shi extract, the anges that take place in the smoking process and quantitative composition, with special reference its detection in finished smoking opium.

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THE COMPOSITION OF THE PACIFIC KELPS.[1]

By J. W. TURRENTINE.

Received Feb. 20, 1912.

Originally the word "kelp" meant the ashes of sea eds a product which was lixiviated for the ex-uction of alkali salts and iodine. Its preparation nstituted an important industry in Scotland and eland during the first half of the nineteenth cen-ry. The term then came to be applied to the plants om which these ashes were prepared; and at pres-t it is used by many to designate all large, dark lored sea weeds. The most definite sense in which e word is used includes all plants belonging to one the families of the brown sea weeds, the Lamina-iceae. Members of this family are found on both e Atlantic and Pacific littoral, but certain ones are culiar to the Pacific. The most important, from an nomic standpoint, because of their size and re-rkable content of potassium salts, are the giant lps. While the various varieties may grow from o to twelve feet in height, the giant kelps are found from thirty to two hundred feet in length and have been observed as long as fifteen hundred feet.

Comparatively little is known concerning the composition of kelps, especially the Pacific kelps. The non-volatile residues of the incinerated plant can be analyzed easily, but to determine the relationships and the combinations existing between the so-called inorganic and the organic constituents of the live plant is not a simple matter.

The composition of the Pacific kelps has been studied by Mr. David M. Balch, of Coronado Beach, Cal., the pioneer investigator of these kelps, whose interesting article on that subject appeared in THIS JOURNAL.[1] He has analyzed the giant kelps of the northern and southern Pacific coast of the United States, the *Nereocystis luetkeana*, and the *Macrocystis pyrifera* and *Pelagophycus porra*. Within the last few days he has submitted to this Bureau analyses of various other genuses from the Puget Sound region.

Samples.—Specimens of various kelps, 80 in all, were collected for analysis from certain points of Alaska by Mr. E. C. Johnston, of the "Albatross;" from Puget Sound (San Juan Co.), Wash., by Prof. G. B. Rigg, of the University of Washington; from the region of Monterey Bay, Cal., by Prof. F. M. MacFarland, of the Leland Stanford, Jr., University; and from the vicinity of San Diego, Cal., by Captain W. C. Crandall, of the La Jolla Marine Biological Station. These embraced about thirty different varieties of kelps and included specimens of the same varieties from different localities, of the same variety at different ages, and of different parts of the same plant. Those from Alaska were mostly of the smaller varieties and were made up of the entire plant; those from Puget Sound represented various varieties, large and small, and consisted of the entire plant or of special parts of the plants, cut into small pieces and transmitted in the dry state, in glass jars; the same statements apply also to those from Monterey Bay. Specimens from San Diego consisted of part of the two kelps, Macrocystis and Pelagophycus. They were partially dried and put in canvas sample sacks for transmittal. Further drying took place in transit and in the laboratory, as a result of which the specimens were in the form of hard and compact masses, or balls.

In sampling, particular care was taken to distribute throughout the whole sample the salts which had crystallized on the surface of the plants in drying and had subsequently fallen off. In some instances it was found more expedient to grind the entire specimen, thus obviating an arbitrary distribution of the effloresced salts.

Drying and Grinding.—The samples chosen were dried, at 103° C., for at least seven hours. They were then ground in an iron mortar. If hard and woody, they were ground finally to extreme fineness in a ball mill, while, if thin and papery, they were ground with ease in the mortar to the desired fineness,—to pass a sieve of sixteen apertures per linear inch.

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[1] Balch, THIS JOURNAL, **1**, 777 (1909).

Method of Analysis.—The method of analysis here described, while possibly faulty in some particulars, was adopted because of the speed with which analyses would be made thereby. Samples of 0.5 g. or thereabouts, were weighed directly into tared platinum crucibles. The crucibles were then placed on an asbestos covered gauze and heated to a temperature below dull redness, when destructive distillation took place. The gases evolved at the mouths of the crucibles were ignited. On the disappearance of the flame the material was thoroughly stirred, with further heating, until all tarry matter had been driven off. Charcoal remained, black or gray in color, and in the form of a loose powder, if the temperature had not been carried too high. The char was transferred to a 200 cc. beaker containing 50 cc. water, the beaker was covered and the solution evaporated to less than 25 cc. The resulting solution was filtered free of solid matter (the filtrate being caught in a platinum dish), the char washed by decantation with hot water, then transferred to the filter and further washed. To the filtrate was added a small volume of ammonium carbonate solution to precipitate calcium carbonate, and it was then evaporated to dryness on a steam bath. Ammonium salts were expelled by heating for an instant to dull redness. The residue was taken up with water and the resulting solution filtered into tared platinum dishes; hydrochloric acid was added, the solution evaporated to dryness on a steam bath, the dishes and their contents were heated again for an instant to dull redness and cooled in a desiccator. The weights of the solids were taken as *soluble salts*.

This procedure was adopted in order that the salts obtained might represent as closely as possible the actual content of soluble salts of the charred kelp. To have converted them into sulfates by the addition of sulfuric acid to the lixiviate would have lessened the liability of loss of potassium salts through volatilization, but would have changed materially the weight of the soluble salts. Where no value is attached to knowledge of the total content of soluble salts, or when one is content to calculate the total soluble salts from a determination of the potassium, sodium, chlorine and sulfate, the latter procedure is to be recommended.

The soluble salts were dissolved in water, the solutions transferred to graduated flasks and diluted to 50 cc. Portions of this, 10 cc. in volume, were subsequently analyzed for potassium by the chlorplatinic acid method.

The residue of charcoal left on the filter after the final filtration, together with the precipitate caught by the second filtration, was ignited to whiteness. The weight was recorded as *ash*.

The sum of the weights of the soluble salts and of the ash when subtracted from the weight of the sample gives a value which represents the matter which has been volatilized. The value is recorded as *organic matter*.

For the determination of iodine, two-gram samples were charred and lixiviated in the manner already described. Iodine was determined in this solution by an adaptation of the method of Bray and MacKay[1]. The filtered solution was transferred to a separatory funnel of 250 cc. capacity, containing 10 cc. of a solution of sulfuric acid (1 cc. conc. H_2SO_4: 9 cc. H_2O) and 10–15 cc. carbon tetrachloride. The solution was titrated with a solution of potassium permanganate previously standardized against pure potassium iodide, the manipulation during the standardization being identical with that employed in the actual analyses. From the solution undergoing titration the liberated iodine was removed as fast as formed by shaking with the carbon tetrachloride. Persistence in the solution of the pink color of the permanganate was taken as the end point.

It should be pointed out that the iodide solution titrated by permanganate must be free from other substances liable to oxidation under the conditions observed. In the ignition of kelps the sulfur present is liable to appear as sulfide if the ignition be carried on at too high a temperature and in an atmosphere depleted of oxygen. Such a result has not been observed, however, as coming from the distillation of kelp, and it is believed that when the distillation has been conducted in an open crucible and with thorough stirring, the absence of other reducing agents (than iodides), both organic and inorganic, is assured. This belief was borne out in the analysis by the fact that the first drop of permanganate liberated iodine, distinctly visible in the solution, and with the complete setting free of the iodine, the next drop or two gave the end point. Whether the above manner of preparing the solution for titration insured the complete recovery of all the iodine is not known. The determination of iodine in organic matter by the Carius method was too difficult, considering the large number of kelp samples analyzed. In the distillation, some iodine may have been lost through the oxidation of the iodide. Information on this point will have to be acquired through experimentation rather than conjecture.

In order to determine whether iodides remained in the char in recoverable amounts, the char was ignited to whiteness and the solution of the resulting ash titrated; only negative results were obtained.

Mr. T. C. Trescott, of the Bureau of Chemistry was so kind as to determine the nitrogen content of the various kelps. The analyses were made of the oven-dried samples by the Kjeldahl method.

DISCUSSION OF TABLE OF RESULTS.

In the second column are given the serial numbers of the kelp samples examined. There are four series consisting of four collections of samples secured during the summer of 1911; they are designated by the initial letter of the name of the collector—as, R: Rigg; M: Macfarland; and J: Johnston, with the exception of the Crandall collection, which is designated by the letter S (Station).

In the fourth column are indicated the location from which the samples were taken. In many instances the locus is given with precision. Crandall

[1] *J. Am. Chem. Soc.*, **32**, 1193 (1910).

TABLE I.

B. of S. No.	Serial No.	Name of kelp.	Location.	Description of sample.	Potash (K_2O).	Iodine (I).	Nitrogen (N).	Soluble salts (Na KClSO$_4$).	Sodium salts estimated.	Organic matter.	Ash of lixiviated plant.	KCl.
1	R 1	Nereocystis luetkeana	San Juan Co., Wash.	Stipe	25.7	0.08	1.29	55 9	15 3	41.8	2.3	40.6
2	R 2	Laminaria bullata	"	"	15.9	0.41	1 99	36.8	11 6	57.4	5.8	25.2
3	R 4	Agarum fimbriatum	"		12.2	0.12	1.99	28 7	9 4	60 3	11.0	19.3
4	R 5	Laminaria bullata	"		10.4	0.29	1.90	25.0	8.6	60.4	14.6	16 4
5	R 6	Nereocystis luetkeana	"	Fronds	13.3	0.15	2.52	35.0	14 0	61.5	3.5	21.0
6	R 7	Laminaria saccharina	"		16 9	0.41	1.66	35 6	8.9	47.0	17.4	26.7
7	R 8	Alaria valida	"		9.2	0.08	1.94	26.4	11 9	66.9	6.7	14.5
8	R 9	Nereocystis luetkeana	"	Fronds	23.0	0.17	1.35	51.3	14.9	46.2	2.5	36.4
9	R 10	Desmarestia ligulata, herbacea	"		13.5	0.12	1.73	41.9	20.6	48.3	9.8	21.3
10	R 11	Laminaria bullata	"		11.0	0.35	1.95	26.4	9.0	64.0	9.6	17.4
11	R 12	"	"		16.4	0.41	2.01	37.9	12.0	56.4	5.7	25.9
12	R 13	Laminaria saccharina	"		17.8	0.53	1.76	38.4	10.3	50 3	11 3	28.1
13	R 14	Pleurophycus gardneri	"		6.9	0.12	1.93	26.5	15.6	34.7	8.2	10.9
14	R 15	Fucus evanescens	"		3.1	0.06	1.66	20.1	15.1	75.3	4.1	4.9
15	R 16	Egregia menziesii	"		13.3	0.08	2.35	30.4	9.4	61.2	8.4	21.0
16	R 17	Costaria turneri	"		17.0	trace	. .	39.1	12.2	54.6	6.3	26.9
17	R 18	Agarum fimbriatum	"		12.4	0.07	1.95	29.5	9.9	60.2	10.3	19.6
18	R 19	Desmarestia ligulata, herbacea	"		6.2	0.06	2.25	24.3	14.5	69.7	6.0	9.8
19	R 20	Cymathaere triplicata	"		13.4	0.06	1.40	32.0	11.0	58.3	9 7	21.0
20	R 21	Laminaria saccharina	"		16.4	trace	1.76	36.3	10.4	50.4	13.3	25.9
21	R 22	Nereocystis luetkeana	"	Fronds	16.2	0.15	2.32	40.4	14.8	55.3	4.3	25.6
22	R 23	Fucus evanescens	"		3.1	none	1.59	19.0	14.1	77.0	4.0	4.9
23	R 24	Cymathaere triplicata	"		13.8	trace	1.56	34.6	12.8	59.7	5.7	21.8
24	R 25	Pleurophycus gardneri	"		7.3	0.12	1.85	27.0	15.5	65.0	8.0	11.5
25	R 26	Egregia menziesii	"		10.3	0.07	2.49	32.1	15.8	60.3	7.6	16.3
26	R 27	Postelsia palmaeformis	Neah Bay, Wash.	Fronds	13.9	0.15	1.83	29.9	7.9	64.4	5.7	22.0
27	R 28	Macrocystis pyrifera	"		19.6	0.20	1.81	32.5	1.5	51.5	16.0	31.0
28	R 29	"	"		14.0	0.22	2.18	30.4	7.3	49.6	19.2	22.1
29	R 30	Pterygophora californica	"	Stipe	0.37	....	. . .	14.8	14.2	. . .	5.2	0.59
30	R 32	Postelsia palmaeformis	"	"	20.0	0.17	1.01	41.1	9.5	54.9	4.0	31.6
31	J 1	Rhodymenia palmata linearis	Yakutat, Yakutat Bay, Ala.	Entire plant	2.8	none	....	7.2	2.8	91.0	1.8	4.4
32	J 2	Fucus evanescens macrocephalus	Sitka, Baranof Island, Alaska	"	2.7	none	....	16.3	12.0	81.1	2.6	4.3
33	J 3	Fucus, evanescens, ag. forma	Sitka, Baranof Island, Alaska	"	2.9	(1).	. .	13.9	9.3	82.7	3.4	4.6
34	J 6	Alaria (lanceolata ?)	Biorka Island, Symonds Bay, Alaska	Portion of plant	3 0	0 12	....	13 5	8 8	77.9	8.6	4 7
35	J 7	Macrocystis pyrifera	Biorka Island, Symonds Bay, Alaska	"	3.1	0.23	1.96	25 2	20 3	70.6	4.2	4 9
36	J 8	Cystophyllum geminatum	Biorka Island, Symonds Bay, Alaska	"	7.3	0.26	1.95	27.0	15.5	64.7	8.3	11.5
37	J 9	Alaria lanceolata	Sitka, Baranof Island, Alaska	"	3.4	trace	....	13.5	8.1	79.4	7.1	5.4
38	J 10	Halosaccion glandiformis	Sitka, Baranof Island, Alaska	"	6.5	trace	....	24.1	13.8	70.1	5.8	10.3
39	M 1	Pastelsia palmaeformis	Montara Point, Cal.	Dried stems	22.8	0.09	0.94	44.5	8.5	52.3	3.2	36.0
40	M 2	Macrocystis pyrifera	Monterey Bay, Cal.		18.3	0.26	2.32	35.7	6.8	57.0	7.3	28.9
41	M 3	Egregia menziesii	Point Pinos, Cal.		11.9	0.12	2.25	27.7	8.9	65.6	6.7	18.8
42	M 4	Macrocystis pyrifera	Off Point Aulon, Cal.		23.0	0.32	1.83	48.3	7.0	51.2	5.5	36.3
43	M 5	Fucus furcatus	Point Alones, Cal.		4.9	trace	1.42	22.5	14.8	73.2	4.3	7.7
44	M 6	Postelsia palmaeformis	Montara Point, Cal.	Fronds	9.7	0.15	1.40	29.7	14.4	66.0	4.3	15.3
45	M 7	Gigartina radula	Monterey Bay, Cal.		3.9	trace	2.18	24.5	18.3	72.1	3.4	6.2
46	M 8	Fucus evanescens	Point Alones, Cal.		5.6	0.13	1.53	20.5	11.7	75.1	4.4	8.8
47	M 9	Nereocystis luetkeana	Point Pinos, Cal.	Thallus	19.4	0.12	1.70	42.8	12.1	53.1	4.1	30.7
48	M 10	Dictoneuron californicum	Point Pinos, Cal.		15.3	0.09	2.11	33.1	8.9	60.0	6.9	24.2
49	M 11	Costaria turneri	Point Alones, Cal.		14.4	trace	2.10	30.5	7.7	61.0	8.5	22.8
50	M 12	Nereocystis luetkeana	Off Point Pinos, Cal.	Stipes and float	26.1	0.15	1.12	55.5	14.3	40.6	3.9	41.2
51	M 13	Gigantina spinosa	Monterey Bay, Cal.		9.2	trace	1.84	25.9	14.3	70.5	3.6	14.5
52	M 14	Laminaria andersonii	Near Point Pinos, Cal.	Stipes and fronds	6.3	0.6	1.77	19.4	9 4	45.8	4.8	10.0
53	S 1	Macrocystis pyrifera	Station 1		15.7	0.15	0.90	35 0	10.1	60.9	4.1	24.9
54	S 2	"	Station 2		13.4	0.23	0.74	31.2	10.0	62.9	5.9	21.2
55	S 3	"	Station 3		13.4	0.29	1.17	29.3	8.1	66.7	4.0	21.2
56	S 4	"	Station 4		13.6	0.38	1.04	30.6	8.2	64.4	5.0	21.4
57	S 5	Pelagophycus porra	Station 5		12.1	0.27	1.10	29.6	10.5	65.5	4.9	19.1
58	S 5 A	Macrocystis pyrifera	"		12.5	0.24	0 81	28.8	9.0	67.3	3.9	19.8
59	S 6	"	Station 6		13.7	0.29	0 95	30.2	8.5	63 7	6.1	21.7
60	S 7	"	Station 7		12.3	0.2	0.98	28.9	9.5	66.2	4.9	19.4
61	S 8	"	Station 8		12.1	0.17	1.56	29.0	9.9	61.8	9.2	19.1
62	S 9	"	Station 9		12.9	0.17	0.83	28.5	8.1	64.8	6.7	20.4
63	S 9 A	"	"		9.8	0.32	0.9	31 2	15.7	65.1	4.7	15.5
64	S 10	"	Station 10		16.7	0 17	0.995	36.6	10.2	56.7	6.7	26.4
65	S 11	"	Station 11		14.1	0.29	0.898	32.2	9.	63.5	4.3	22.3
66	S 12	"	Station 12		16.9	0.26	1.35	36.3	9.6	58.3	5.4	26.7
67	S 13	"	Station 13		12.6	0.26	0 95	30.4	10.5	64.4	5.2	19.6
68	S 14	"	Station 14		17.4	0.32	1.57	44.1	16.6	49.4	6.5	27.5
69	S 15	"	Station 15		17.4	0.26	1.09	39.0	11.5	55.7	5.3	27.5
70	S 16	"	Station 16		16.4	0.29	1.54	41.2	15.3	50 6	8.1	25.9
71	S 16 A	"	"		8 4	0.41	1.01	22.1	8.8	71.7	6.2	13.3
72	S 17	Pelagophycus porra	Station 17	Young plant	19.5	0.5	1 01	41.0	10.2	52.4	6.6	30.8
73	S 17 A	"	"	Leaves	15.6	0.27	1.63	37.38	12.8	56.2	6.4	24.6
74	S 17 B	"	"	Bulbs	29 9	0.35	0.53	60.6	13.1	36.4	3.0	47 5
75	S 17 C	Macrocystis pyrifera	"	Stems	18.7	0.38	1.24	40.3	10 7	54.4	5.3	29.6
76	S 17 C X	"	"	Stems and leaves	12 4	0.38	1.04	28.3	8.7	64.8	6.9	19.6
77	S 18	"	Station 18		10 6	0.19	0.53	28.6	11.9	61.3	10.1	16.7
78	S 19	"	Station 19			0.41		. .	. .	.		
79	S 19 X	"	"		7.2	0.32	0 53	19.2	7.7	76.3	4 5	11.5
80	S 20	"	Station 20		.	0.38	0.62	27.95	. . .	67.0	5.1	.
81	S 20 A	Pelagophycus porra	"		22.4	0.41	0.69	46.8	12.4	48.4	4.8	34.4

(1) Faint trace.

has marked as Stations the points from which his samples were collected, and has "placed" each station in degrees, minutes and seconds, as follows:

Station	1	Off Pt. Loma	32° 39′ 30″ 117° 16′
"	2	Off Bird Rock	32° 45′ 6″ 117° 17′
"	3.	La Jolla	32° 51′ 30″ 117° 16′ 6″
"	4	San Juan	33° 27′ 117° 43′ 6″
"	5.	Pt Fermin	33° 43′ 12″ 118° 21′ 30″
"	6.	Malaga Cove	33° 48′ 36″ 118° 24′ 26″
"	7.	Bet. Pt. Gorda & Las Pitas	34° 14′ 20″ 119° 15′
"	8.	Summerland	34° 24′ 15″ 119° 35′ 45″
"	9.	Santa Barbara, outside edge	34° 24′ 119° 40′ 36″
"	9a.	Santa Barbara, inside edge	
"	10.	St. Naples	34° 25′ 12″ 119° 56′ 45″
"	11.	C. Quemada	34° 27′ 24″ 120° 7′
"	12.	Little Caxo	34° 26′ 15″ 120° 24′ 30″
"	13.	Anacopa, Wreck of W. Scott	34° 0′ 55″ 119° 23′ 22″
"	14.	Santa Cruz, Gull Is	33° 56′ 30″ 119° 49′ 15″
"	15.	San Miguel, Cuyler Cove	34° 3′ 10″ 120° 21′
"	16.	Tylers Bight, San Miguel	34° 0′ 33″ 120° 24′ 15″
"	16a.	Johnstons Lee, Santa Rosa	33° 53′ 45″ 126° 0′ 0″
"	17.	St. Nicholas	33° 16′ 50″ 119° 1′ 6″
"	17a.	St. Nicholas Is	33° 16′ 50″ 119° 37′ 45″
"	18.	Santa Barbara Is	33° 28′ 6″ 119° 1′ 6″
"	19.	Clemente, West side	32° 57′ 9″ 118° 35′ 12″
"	20.	Clemente, Smugglers Cove	32° 48′ 12″ 118° 23′

Where no statement is made concerning the nature of the sample it should be understood that it was composed of the leafy parts of a large variety, or the entire plant, of a young, smaller kelp. Thus the samples of the southern Macrocystis consisted, in practically every instance, of branches, bearing fronds and floats.

The soluble salts, given in the ninth column, represent the weights of the combined sodium and potassium sulfates and chlorides and the soluble magnesium salts. The solution from which these had been precipitated had been treated with ammonium carbonate and were probably free from calcium salts.

In the test analyses it was found that there were but negligible amounts of both calcium and magnesium salts in the solution obtained on lixiviating the charred kelp. Whether it is safe to conclude that the lixiviate from the char of every kelp is so free from calcium and magnesium salts is an open question. It is the writer's opinion that the question is answerable in the affirmative. In very rare cases did the addition of ammonium carbonate to the lixiviate produce any precipitation of calcium carbonate; this shows a constant freedom from calcium salts and may be taken, by analogy, as an indication of a similar absence of magnesium salts.

In the tenth column the estimated sodium salts are recorded. These values are mere estimates and most probably are inaccurate. They are obtained by subtracting the percentage of potassium chloride from the percentage of soluble salts; were both potassium and sodium present as chloride alone in the absence of magnesium, these values would be accurate. It has been shown that sulphates are present in variable amounts. To calculate the potassium to chloride when it is present wholly or in part as sulfate, throws the entire error thereby introduced upon the sodium, making it appear disproportionately large.

When the average potassium chloride content of the twenty-nine samples of the northern kelps (from Puget Sound) is compared with that of the twenty-seven samples of the southern (from the region of San Diego), the respective values being 21.3 per cent and 23.4 per cent., it appears that the content of the southern plants exceeds that of the northern. It is seen, however, that the northern collection comprises numerous varieties not included in the southern. Choosing the four varieties in the northern collection which occur in the greatest quantities (the genuses Nereocystis, Macrocystis, Postelsia, and Egregia nine specimens), the average KCl content is 25.7 per cent Drawing the comparison still closer and comparing the two genuses of the North considered as a commercial source of potash, Nereocystis and Macrocystis, with the two of the south likewise so considered, Macrocystis and Pelagophycus, the average content of the former (six specimens) is 29.4 per cent. KCl, a value considerably in excess of that obtained for the southern varieties (23.4 per cent.). The average content of the two specimens of Macrocystis from Puget Sound is 26.5 per cent.; that of the twenty-two specimens from the South is 21.6 per cent. It is hardly just to draw conclusions from the last comparison; but considered as a whole, indications are that the northern kelps are richer in KCl than the southern.

The average iodine content of the thirty specimens from Puget Sound is 0.155 per cent. and of the four main varieties (ten specimens) is 0.14 per cent. The average of six specimens of the two giant kelps, the Nereocystis and the Macrocystis, is 0.16 per cent The average percentage content of the southern kelps is 0.29, a value nearly twice that from the northern kelps. From these figures it appears safe to conclude that the northern kelps are richer in potash but poorer in iodine than the southern kelps.

The average KCl and I content of the three giant kelps as derived from the table are:

	Percentage KCl.	I.
Nereocystis	32.6 (av. of 6)	0.14 (av. of 6
Macrocystis	22.2 (av. of 27)	0.27 (av. of 29
Pelagophycus	31.3 (av. of 5)	0.36 (av. of 5

In addition to the variations in composition between the varieties of kelps it will be noted that there is a marked variation between members of the same genus from different localities and from the same locality. There is also a variation strikingly shown in the case of Pelagophycus (Nos. 72, 73 and 74

etween the different parts of a single plant. These ifferences have been pointed out by Balch.[1]

Phosphorus.—Phosphorus was determined by the fficial method proposed for the determination of hat element in organic substances. The results obained are given in the following table:

TABLE II.—ANALYSES BY J. A. CULLEN.

No.	Serial No.	Name of Kelp.	Location.	P_2O_5. Per cent.
1	R 1	*Nereocystis luetkeana*	San Juan Co., Wash.	0.70
2	R 16	*Egregia menziesii*	"	1.79
3	R 27	*Postelsia palmaeformis*	Neah Bay, Wash.	1.04
4	R 28	*Macrocystis pyrifera*	"	0.81
5	M 2	*Macrocystis pyrifera*	Monterey Bay, Cal.	1.84
6	M 9	*Nereocystis luetkeana*	Point Pinos, Cal.	0.83
7	S 10	*Macrocystis pyrifera*	St. Naples, Cal.	0.66
8	S 15	*Macrocystis pyrifera*	San Miguel, Cuyler Cove, Cal.	0.71
9	S 17 B	*Pelagophycus porra*	St. Nicholas, Cal.	0.51

Sulfur.—Sulfur was determined as barium sulfate n the lixiviate of the charred kelp and ash comined. The char from two-gram samples was lixiated in the manner described in a foregoing pararaph and then burned to whiteness. The ash was issolved in hydrochloric acid and the resulting olution evaporated to dryness to dehydrate silicic cid. The residue was taken up with acid, the solution filtered and the filtrate added to the lixiviate rom the char. Sulfuric acid was determined in the ombined solution in the usual way. The results re recorded in the following table:

TABLE III.

No.	Serial No.	Name of Kelp.	Source.	SO_3. Per cent.
1	R 6	*Nereocystis luetkeana*	San Juan Co., Wash.	1.68
2	R 29	*Macrocystis pyrifera*	Neah Bay, Wash.	2.24
3	M 4	*Macrocystis pyrifera*	Off Pt. Aulon, Cal.	2.42
4	M 12	*Nereocystis luetkeana*	Off Pt. Pinos, Cal.	1.08
5	S 14	*Macrocystis pyrifera*	Santa Cruz, Gull Is.	3.45
6	S 20 A	*Pelagophycus porra*	Clemente, Smugglers Cove, Cal.	2.33

Organic Constituents.—Little or nothing is known oncerning the organic constituents of the Pacific elps. From the figures in Table I, it can be seen hat the organic matter in them rarely falls below o per cent. or exceeds 75 per cent. On the average hey contain about 1.5 per cent. of nitrogen which, calculated to protein by the usual factor, is equivant to 9.4 per cent. protein. This value is about qual to that of other sea weeds examined for that onstituent.

Our knowledge concerning the organic constituents sea algae in general, from which we may derive me idea of what may occur in the Pacific kelps, ay be summed up thus: The simple sugars have en identified in certain algae, but they are of rare nd scanty occurrence; starch has been said to occur some varieties, but its identification has not been bstantiated; mannan and levulose are of rare occrrence; galactan is common and abundant, and penfsan is the most abundant of all.

BUREAU OF SOILS,
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WASHINGTON, D. C.

[1] *Loc. cit.*

A NOTE ON THE DETERMINATION OF IODIDES BY DIRECT TITRATION.[1]

By J. W. TURRENTINE

Received February 20, 1912.

Bray and MacKay[2] have described a method for the determination of iodides in the presence of bromides and chlorides wherein the iodine is liberated from the iodides by standardized potassium permanganate, added titrimetrically, and is extracted as formed by shaking with successive portions of carbon tetrachloride. When the last of the iodine has been set free, the carbon tetrachloride extract is run off from the supernatant aqueous layer and is shaken with a solution of potassium iodide for the extraction of the iodine. The potassium iodide extract is titrated in the usual way with standard thiosulfate solution.

In the analysis of kelps for iodine a method was sought which would admit of the determination of small amounts of iodide with the minimum expenditure of time. For this purpose the initial liberation of the iodine was effected by standardized potassium permanganate and the amount of iodide thereby determined. The method then became strictly a direct titration of iodide in the presence of bromide and chloride. The results obtained were satisfactorily consistent, and the rapidity with which determinations could be made by means of it was such that this account of the method is deemed warranted.

The permanganate solution was standardized against solutions of potassium iodide of known concentration (1.0 g. KI to 1000 cc. H_2O), the iodide of which had been purified by recrystallization and thorough drying.

Portions of the standard iodide solution were transferred, in graduated pipets, to a 250 cc. dropping funnel; 15 cc. of sulphuric acid solution (10 cc. conc. H_2SO_4 to 90 cc. H_2O) and 15 cc. of carbon tetrachloride were added. For the removal of reducing agents, the carbon tetrachloride had been treated for several hours with iodine which was subsequently removed by shaking with sodium thiosulfate solution.

The solution of the permanganate was run in from a burette, and as the titration proceeded the liberated iodine was removed from the aqueous layer by shaking. With the decrease in the concentration of the iodide in this layer, the solubility of the iodine therein decreased, until, as the end of the titration was approached, the solution became entirely colorless. The persistence for one minute of the pink color of the permanganate was taken as the end point. The procedure was identical with that observed in the actual analysis.

At first the color of the carbon tetrachloride layer caused some trouble in discerning the end point, but with experience the trouble disappeared.

Bray and MacKay have pointed out that in the direct titration of iodides by a permanganate solution there is an error introduced by the incomplete reduction of the last of the permanganate to a form intermediate between the heptavalent and the divalent condition. This would appear to be due to the de-

[1] Published by permission of the Secretary of Agriculture.

[2] *J. Am. Chem. Soc.*, **32**, 1193 (1910).

crease in the active mass of the iodide, since it is not observable in the presence of an excess of that substance. For a definite amount of the permanganate, then, the intermediate form of the manganese should not be present in the solution until after the iodide had been reduced to a definite concentration. When the concentration of the former is very low (as is normally the case as the end of the titration is approached), that of the iodide likewise would be very low before the reaction leading to the formation of the intermediate manganese compound appeared. In the titration, accordingly, the incomplete reduction does not occur until a definite and very low concentration of the iodide is reached. This point, it follows—since the reaction is irreversible—must be independent of the original active mass of the iodide. For that reason the error should be a constant rather than a variable one; and if the latter, certainly a correction could be introduced whereby it would be neutralized.

It was observed that values obtained for small amounts of iodide undergoing titration were relatively greater than those obtained for larger amounts. When the blank solutions were titrated in the absence of the iodide, it was found that a small amount of the permanganate (0.2 cc.) was reduced. As this was not observable in the absence of the carbon tetrachloride, the reduction of the permanganate was attributed to the carbon tetrachloride, or to some constituent thereof. When a correction was made for this error the values obtained from the titration of the various volumes of standard iodide were found to be concordant within the probable error of experimentation. These values are given in the following table:

No.	Cc. KI.	Cc. $KMnO_4$ corrected.	KI value per cc. $KMnO_4$ corrected.
1	10	1.6	0.00625
2	10	1.6	0.00625
3	10	1.55	0.00645
4	10	1.5	0.00666
5	10	1.6	0.00625
6	10	1.55	0.00645
7	20	3.2	0.00625
8	20	3.2	0.00625
9	20	3.3	0.00606
10	25	4.05	0.00617
11	40	6.55	0.00611
12	40	6.5	0.00615
13	40	6.5	0.00615
14	100	16.5	0.00602
		Mean,	0.00624

The range in values in iodide of the solutions titrated in the standardization was the same as that which was expected to be found in the substances to be analyzed. For that reason they cover only a small range. Whether the method is applicable to the determination of larger amounts of iodide can not be said, but *a priori* considerations indicate that it may be employed. It should only be necessary to remove the iodide with successive portions of carbon tetrachloride in order that that layer might not become too concentrated in iodine. Whether new corrections would have to be introduced or not could be determined experimentally.

The permanganate solution was standardized with solutions containing no chlorides or bromides, while the solutions analyzed contained large amounts of chlorides and presumably some bromides. Bromides in small amounts are commonly found among the saline constituents of sea algae. Whether they were present in the specimens analyzed has not been determined. In this particular, then, the conditions existing during the standardization were not strictly reproduced in the analysis. However, the authors whose method is here applied have explained the conditions under which chlorides and bromides are liable to introduce an error in the determination of iodide and, it is believed, those conditions were strictly observed in the adaptation of the method to the analysis of kelps.

It is a truism that any titration method is reliable in which the solutions employed are standardized against the compound which is to be determined, provided the standardization and the analyses be made under identical conditions.

BUREAU OF SOILS,
U. S. DEPARTMENT OF AGRICULTURE,
WASHINGTON, D. C.

DETERMINATION OF TOTAL POTASSIUM IN MINERALS.

By CHARLES J. SCHOLLENBERGER.

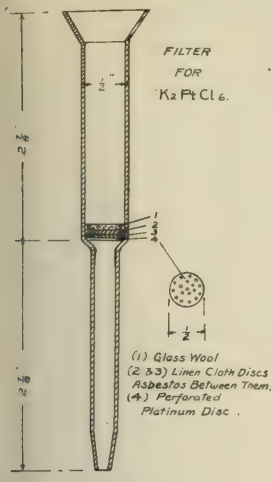
Received December 18, 1911.

In very many instances only the percentage of potassium in a sample is required to be determined, while the amount of sodium present is a matter of indifference. In such cases, the method of J. Lawrence Smith is long and tedious; the modification of Smith's method, described by Pettit and Ystgard in Proceedings of the Association of Official Agricultural Chemists (1906), while shorter, leaves much to be desired. It has the disadvantage that a large amount of an alkaline solution must be evaporated in glass, with the attendant liability of contamination. The calcium carbonate which separates during this evaporation is non-crystalline, adherent, and difficult to wash. Even after filtration, much silica remains in the solution, causing trouble in later operations. In order to overcome these difficulties, and, if possible, to further shorten the time required for a determination, the following method was worked out in this laboratory:

Proceed as in the regular Smith method for total alkalies, until the filtrate from washing out the alkalies from the fusion is obtained. To this add a moderate excess of hydrochloric acid and evaporate to dryness on a steam bath, remote from ammonia fumes. Take up with about 2 cc. of concentrated hydrochloric acid and 25 cc. of hot water, and filter through a special suction filter into a 150 cc. beaker, washing the large beaker and filter well. Add the proper amount of hydrochloroplatinic acid solution, and evaporate on steam bath until of a semi-solid consistency. The large amount of calcium chloride present crystallizes out on cooling, but is readily soluble in acidulated alcohol. The crystalline precipitate of the potassium chloroplatinate is washed with acidulated alcohol,[1] Gladding wash, and 80 per cent. alcohol, on a filter designed especially for this work. After drying to re-

[1] *Jour. Am. Chem. Soc.*, **20**, 341.

move alcohol, the precipitate is dissolved in hot water, the solution being received in a tared platinum dish, and after evaporation, dried and weighed.



The special filter mentioned was designed by Professor J. W. Ames, chief of the chemistry department, and is of the form and dimensions shown in the drawing; the filtering medium, supported by a perforated disc of platinum, consists of a neatly fitting circular piece of linen cloth, a small amount of purified asbestos, and a small plug of glass wool, to prevent the asbestos being disturbed.

The filter is intended to be used with suction; it has many advantages over a funnel and paper, or a Gooch crucible, filtering much more rapidly, and being much more easily washed free from soluble salts, by reason of the decreased area of the filtering medium.

The advantages gained by using this method of filtration are increased accuracy of results, as well as a great saving of labor and time.

The above-described method has been in use for some time and has given very satisfactory results on several hundred soil samples.

OHIO AGRICULTURAL EXPERIMENT STATION,
WOOSTER, OHIO.

NOTE ON THE NEUTRAL PERMANGANATE METHOD FOR THE AVAILABILITY OF ORGANIC NITROGEN.[1]

By JOHN PHILLIPS STREET.

Received January 12, 1912.

When the neutral permanganate method was devised some years ago by the writer, a series of mixtures of known composition was prepared by which it was possible to determine the availability of the organic nitrogen both in the raw material and when mixed with the usual phosphatic and potassic ingredients of commercial fertilizers. In these mixtures arbitrary amounts of acid phosphate and muriate of potash were used, the total weight of the mixtures always equaling 50 grams, the acid phosphate varying from 10 to 34.5 grams, and the muriate being constant at 10 grams. The mixtures, with one exception, each contained an equivalent of 1.50 per cent. of organic nitrogen in varying forms. The agreement in availabilities of the organic form, when used alone and when mixed, was considered quite satisfactory; at any rate the figures obtained were sufficient, in the writer's estimation, to allow of a differentiation between the valuable and the relatively useless forms of organic ammoniates.[2]

[1] Presented at the American Chemical Society Meeting at Washington, D. C., December, 1911.

[2] THIS JOURNAL, **2**, 312 (1910).

A more extended series of tests, however, has shown that the method as originally published might give misleading results, which in certain cases would be most unfair to high-grade materials. In other words, under certain conditions, a high-grade material like dried blood, which showed a high permanganate availability unmixed, when mixed with acid phosphate and muriate of potash showed availabilities which would class it with garbage tankage and only a little above peat. Apparently the cause of this discrepancy in results lay either with the acid phosphate or the potash. Accordingly, another series of mixtures were made in which the quantity of these ingredients was varied, while the amount of organic nitrogen was kept constant at 0.0450 gram. These experiments showed at once that the muriate of potash had no effect on the results. A sample of dried blood which unmixed showed an availability of 97, when mixed with muriate showed 95 and 96. This same blood, however, when mixed with 2 grams of acid phosphate, showed only 90, and with 4 grams only 59. In three samples of blood the presence of 4 grams of acid phosphate reduced the availabilities from 96, 94 and 96 to 53, 70 and 67, respectively. While this discrepancy was most marked in the case of dried blood, a decreased availability was also noted in tankage, fish, hide and skin meal, tartar pomace, solubilized organic nitrogen and peat. With knuckle bone and cottonseed-meal the acid phosphate seemed to have less effect, and with garbage tankage the availability of the nitrogen in the mixture was, as has always been my experience, considerably higher than in the raw material.

It was thought at first that the relatively large amount of acid phosphate (4 grams), compared with the charge of dried blood (0.34 gram), prevented complete action of the permanganate. Experiments carried on by Mr. J. E. Breckenridge, in which the permanganate mixture was agitated much more frequently than directed in the method, however, gave no better results. Thinking that the acidity of the acid phosphate might be the determining factor, another series of tests were carried out in which one gram of sodium carbonate was added just prior to the introduction of the permanganate solution. The results obtained were most satisfactory, as the table shows. A 96 blood with 2 grams of acid phosphate showed 96, with 4 grams, 90. A 91 tankage with the same amounts of acid phosphate showed 94 and 85. A 97 bone showed 93; a 93 fish, 92; a 92 cottonseed-meal, 95; a 54 tartar pomace, 48; a 65 solubilized organic nitrogen, 65; a 46 peat, 42. Garbage tankage again showed a high result, the availability increasing from 47 to 68, but even this high figure is too low to mislead any one as to its value.

The writer makes no attempt to explain just what causes these discrepancies. That they exist, however, is an undoubted fact, and the simple modification, at least in the materials tested, appears to give true and reasonable results.

In using the neutral permanganate method, it must be remembered that it is not an absolute method, and that no pretense is made that by it the exact

agricultural value of an organic nitrogenous material may be determined. A long series of tests, however, shows that it does differentiate between the good and the bad materials of generally recognized value like blood, tankage, ground bone, dried fish, cottonseed-meal and castor pomace rarely showing availabilities less than 90, while leather, mora meal, tobacco stems, peat, sheep manure, garbage tankage, tartar pomace, beet root manure and fillerine show availabilities from 17 to 69. The method possesses the further advantages of simplicity of manipulation, of easy maintenance, of uniform conditions (a very important matter) and of measuring a definite chemical action, namely, the amount or organic nitrogen not decomposed by a definite quantity of permanganate of potash solution of fixed and uniform strength, acting for a definite time at a uniform temperature on a definite amount of organic nitrogen. Every condition can be definitely controlled and the personal equation is almost negligible.

The method as now used by the writer is as follows:

	Nitrogenous material.	Acid phosphate.	KCl.	Na_2CO_3.	$KMnO_4$ solubility. Raw material.	$KMnO_4$ solubility. Mixture.
Blood, No. 22160.....	−0.34	2.00	0.50	..	96	83
	−0.34	3.00	0.75	....	96	70
	−0.34	4.00	1.00	..	96	53
	−0.34	2.00	...	1.00	96	96
	−0.34	4.00		1.00	96	90
Blood, No. 24003.....	−0.33	...	1.00	....	97	96
	−0.33	2.00	.		97	90
	−0.33	2.00	1.00	.	97	89
	−0.33	4.00	1.00	.	97	59
Blood, No. 22406.....	0 44	4.00	1.00	..	94	70
Blood, No. 22965.....	0.56	4.00	1.00	....	96	67
Tankage, No. 22346 . . .	−0.96	2.00	0.50	...	91	80
	−0.96	3.00	0.75	..	91	82
	−0.96	4.00	1.00	....	91	78
	−0.96	2.00	.	1.00	91	94
	−0 96	4.00	....	1.00	91	85
Knuckle bone, No. 22360..	−1.17	2.00	0.50	..	97	88
	−1.17	3.00	0.75		97	84
	−1.17	4.00	1 00	.	97	90
	−1.17	4.00	.	1.00	97	93
Fish, No 22667.. . . .	−0.70	2.00	0.50	..	93	89
	−0.70	3.00	0.75	.	93	88
	−0.70	4.00	1 00		93	85
	−0.70	2.00	..	1.00	93	92
Cottonseed-meal, No. 22393.	−0.75	1.95	0.67	.	92	90
	−0.75	2 00		1.00	92	95
Hide and skin meal, No 24009.....	−0 58	2 00	1 00		75	60
	−0 58	4.00	1.00		75	45
Garbage tankage, No. 22383	−2.25	0.75	0.75		47	70
	−2.42	4.00	1.00		47	55
	−2.42	2 00		1.00	47	68
Tartar pomace, No. 24013.	−1.29	4 00	1.00		54	34
	−1.29	4 00	.	1.00	54	48
Solubilized organic nitrogen, No. 23998.....	−0.93	4.00	1.00		65	20
	−0.93	4.00		1.00	65	65
Peat, No. 23392..... .	−1.67	4.00	1.00		46	22
	−1.67	4.00		1.00	46	42
	−1.67	2.00	.	1.00	46	45

MODIFIED NEUTRAL PERMANGANATE METHOD.

Weigh a quantity of the fertilizer, equivalent to 45 mg. of water-insoluble organic nitrogen,[1] on a moistened 11 cm. filter paper, and wash with successive portions of water at room temperature until the filtrates amount to 250 cc. Transfer insoluble residue with 25 cc. of tepid water to a 300 cc. low-form Griffin beaker, add one gm. sodium carbonate and 100 cc. of 2 per cent. permanganate solution. Digest in a steam or hot-water bath for thirty minutes at the temperature of boiling water, covering the beaker with a watch glass and setting well down into the bath so that the level of the liquid in the beaker is below that of the bath. Stir twice at intervals of ten minutes. At the end of the digestion remove from the bath, add 100 cc. of cold water and filter through a heavy 15 cm. folded filter. Wash with cold water, small quantities at a time, until total filtrate amounts to about 400 cc. Determine nitrogen in residue and filter, correcting for the nitrogen of the filter.

[1] Determined by washing one gram of the material on a 11 cm. filter with water at room temperature, to a volume of about 250 cc. Dry and determine nitrogen in the residue, making a correction for the nitrogen in the filter paper if necessary

ACTIVITY OF ORGANIC NITROGEN AS MEASURED BY THE ALKALINE PERMANGANATE METHOD.[1]

By C. H. Jones.

Received January 12, 1912.

During the past year a large amount of work has been done toward securing a quick, reliable laboratory method for determining the activity of organic nitrogen in crude stock and commercial fertilizers.

A committee of Experiment Station Chemists, appointed in March, 1910, has been given opportunity to observe the methods employed in "wet mixing" and to secure samples of both the raw materials used and the finished product. These have been tested by laboratory methods and vegetation experiments, and, as a result of this work, the following method, perfected by the writer, and known as the Alkaline Permanganate Method, was adopted in March, 1911, by the directors of the Experiment Stations of New York, New Jersey, and the New England States.

ALKALINE PERMANGANATE METHOD FOR ORGANIC NITROGEN ACTIVITY.

(1) *With Mixed Fertilizers.*—Transfer an amount of material equivalent to *50 milligrams of water insoluble organic nitrogen*[2] to a filter paper and wash with successive portions of water at room temperature until the filtrate amounts to about 250 cc. When it is found necessary to use four or more grams of the original material to secure the 50 milligrams of water insoluble nitrogen, *i. e.*, when the percentage of water insoluble nitrogen is 1.25 or less, weigh the required amount into a small beaker, wash by decantation, finally transfer to the filter and finish the extraction as previously directed. When a relatively large amount (7 to 10 grams of a fertilizer) is to be extracted it is desirable to weigh out duplicate portions. One is used for the determination of nitrogen activity by the alkaline permanganate method, and the other is Kjeldahled for its nitrogen content. Compare the latter figure with the result previously obtained from the two gram extraction (see footnote) and in case of any marked discrepancy, *i. e.*, over 0.05 per cent. of nitrogen, calculate the nitrogen activity on the basis of the exact nitrogen equivalent used.

(2) *With Raw Materials.*—Transfer an amount of

[1] Presented at the American Chemical Society Meeting at Washington, D. C., December, 1911.

[2] Determined by extracting 2 grams of the material on a filter paper with water at room temperature, until the filtrate amounts to about 250 cc. Determine nitrogen in the residue, making a correction for the nitrogen in the filter paper if necessary.

material equivalent to *50 milligrams of water insoluble organic nitrogen*[1] to a small mortar, add about 2 grams powdered rock phosphate, mix thoroughly, transfer to a filter paper and wash with successive portions of water at room temperature until the filtrate amounts to about 250 cc. When much oil or fat is present, it is well to wash somewhat with ether before extracting with water. Dry the residue at a temperature not exceeding 80° C. and *transfer from the filter* to a 500–600 cc. Kjeldahl distillation flask (round bottom preferred, but, if flat bottom is used, incline at an angle of 30°). Add 20 cc. water, 15 to 20 small glass beads to prevent bumping, and 100 cc. alkaline permanganate solution (25 grams pure potassium permanganate and 150 grams sodium hydroxide, separately *dissolved* in water, the solutions cooled, mixed and made to volume of one liter). Connect with an upright condenser to which a receiver containing standard acid has been attached. Digest slowly, *below distillation point, with very low flame*, using coarse wire gauze and asbestos paper between flask and flame, for *at least 30 minutes. Gradually* raise the temperature and when danger (if any) from frothing *has ceased*, distil *until* 95 cc. of distillate are obtained, and titrate as usual. In cases where a tendency to froth is noticed, lengthen the *digestion* period and no trouble will be experienced when the distillation is begun. During the digestion, gently rotate the flask occasionally, particularly if the material shows a tendency to adhere to the sides. It is recommended that as nearly as possible 90 minutes be taken for the digestion and distillation. The nitrogen thus obtained is the *active water insoluble organic nitrogen.*

The results are expressed in the following form:

1. Nitrogen in nitrates.
2. Nitrogen in ammonium salts.
3. Water soluble organic nitrogen.
4. Active insoluble organic nitrogen.
5. Inactive insoluble organic nitrogen.
6. Total nitrogen.

The first two divisions include the mineral forms of nitrogen derived mainly from nitrate of soda and sulphate of ammonia. Both are water soluble and readily available for plant growth.

The third division includes that portion of the organic nitrogen which is soluble in water. It is considered highly available as plant food.

The fourth division comprises that portion of the water insoluble organic nitrogen which is liberated by the alkaline permanganate method. It is likewise available for plant food, and hence is termed "Active."

The fifth division, listed as "Inactive Insoluble Organic Nitrogen" is that portion unaffected by the alkaline permanganate treatment and is of little value for the immediate use of plants. It is, therefore, rightly termed "Inactive."

In this connection it should be mentioned that results secured by the alkaline permanganate method have been confirmed by vegetation trials on a considerable number of prominent crude stock nitrogenous materials, as well as on the water insoluble portion of many high and low grade commercial fertilizers.

To fully illustrate the adaptability of the method, and form used to express the results, the accompanying table has been prepared, giving results by the alkaline permanganate method on crude stock, commercial fertilizers and mixtures of known composition. The samples reported have been carefully selected from a large list and may be regarded as typical of the ordinary materials now met with in the fertilizer industry.

The interpretation of results, when the suggested form is used, is very simple. It is, however, necessary at the outset to understand that results by the laboratory method under discussion deal wholly with the *quality*, not quantity, of the *organic nitrogen* and that any amount of nitrate or ammonia has no effect on the activity of the organic nitrogen present.

To determine whether the organic nitrogen has been derived from materials of known high availability, *i. e.*, blood, tankage, cottonseed-meal, etc., or from more inert or slowly available sources, *i. e.*, garbage tankage, peat, etc., a comparison of the columns headed "Active" and "Inactive" will at once tell the story. *Organic nitrogen is derived from high grade materials in proportion as the stated percentage in the "Active" column is greater than that in the "Inactive" column and its class and its availability as plant food can be accurately inferred by then noting the relative quantity of water soluble organic nitrogen present.*

The availability of the total nitrogen in a fertilizer should not be confused with the availability of the organic nitrogen present. Total availability can easily be calculated by assuming nitrates and ammonia salts to be entirely available.

To further illustrate the interpretation of results, let us consider some of the individual samples reported in the table.

Crude Stock, Nos. 1–14.

No. 1, Dried Blood. More than twice as much "active" as "inactive" insoluble nitrogen. A high grade material.

No. 2, H. G. Tankage. More than twice as much "active" as "inactive" insoluble nitrogen. Contains a large percentage of water-soluble organic nitrogen which is characteristic of many tankages. High grade.

No. 5, Base Goods (wet mix) made under Station supervision. A small percentage of "active" and "inactive" organic nitrogen, the latter in excess, indicates a small amount of some low grade material. The relatively large water soluble percentage 1.03, which is readily available, is characteristic of the wet mix process and at once places the material in the high grade class.

No. 6, Cottonseed-Meal. "Active" well in excess of "inactive." High grade.

No. 12, Garbage Tankage. "Inactive" more than twice as much as "active." A low grade material.

No. 13, Peat. "Inactive" in excess of "active." A low grade material.

[1] Determined by extracting 2 grams of the material on a filter paper with water at room temperature, until the filtrate amounts to about 250 cc. Determine nitrogen in the residue, making a correction for the nitrogen in the filter paper if necessary.

Commercial Fertilizers, Nos. 15–22.

No. 15. "Active" nearly twice the "inactive" and a generous allowance of water soluble organic nitrogen is present. High grade.

No. 16, "Inactive" greater than "active." A small amount of water soluble organic nitrogen. Poor grade. The large percentage (2.46) of nitrate and ammonia present would make the total availability of the nitrogen in this fertilizer quite high, but does not alter the fact that the organic nitrogen came from low grade sources.

Nos. 25 and 26, "Active" over twice as much as "inactive." High grade.

Nos. 27 to 33 are mixtures of 26 parts base goods (wet mix) No. 5 with 3 parts of eight different organic ammoniates. Nos 27 to 31, owing to excess of "active" over "inactive," are rated as high grade.

In Nos. 32 and 33, the introduction of garbage tankage and peat is in evidence, as shown by the excess of "inactive" over "active."

No. 34. The nitrogen is obtained from dried blood and cottonseed-meal and shows nearly three times as much "active" as "inactive" nitrogen. High grade.

No. 35. The nitrogen is obtained from treated leather, garbage tankage and peat. It shows an excess of "inactive" over "active," and the low grade of the nitrogen material is thus indicated.

TABLE I.

Number	Crude stock. Material.	Nitrogen per cent. In nitrates.	In ammonia salts.	Water soluble organic	Active, water insoluble organic.	Inactive water insoluble organic.	Total.	Organic and volatile matter in the water insoluble material. Per cent.	Per cent. of nitrogen in the organic and volatile matter.
		1.	2.	3.	4.	5.	6.	7.	8.
1	Dried blood	....	0.06	0.25	9.82	4.01	14.14	84.9	16.3
2	High grade tankage	....	0.12	3.75	4.28	1.93	10.06	60.4	10.3
3	Fish	....	0.08	0.40	7.26	2.35	10.29	83.9	11.7
4	Hoof meal	....	0.14	0.94	9.47	4.25	14.80	81.4	16.9
5	Base goods (wet mix)	....	0.25	1.03	0.21	0.34	1.83	12.1	4.5
6	Cottonseed meal	....	0.09	0.54	4.09	2.30	7.02	67.7	9.4
7	Castor pomace	....	0.06	0.82	2.55	1.85	5.28	58.6	7.5
8	Medium tankage	....	0.27	0.92	2.85	1.61	5.65	48.7	9.2
9	Bone meal	....	....	0.59	1.39	0.68	2.66	24.4	8.5
10	Treated leather	....	0.27	0.63	2.88	2.76	6.54	75.2	7.5
11	Charred leather	....	0.04	0.07	0.12	0.79	1.02	22 5	4 0
12	Garbage tankage	....	0.06	0.31	0.84	1.95	3.16	54.9	5.1
13	Peat	....	0.02	0.04	1.24	1.79	3.09	71.5	4.2
14	Mora meal	....	0.03	0.31	0.75	1.60	2.69	51.0	4.6
	Commercial Fertilizers.								
15	Guaranteed 3 per cent. plus nitrogen	....	0.77	1.26	1.30	0.70	4.03	14.7	13.6
16	Guaranteed 3 per cent. plus nitrogen	1.15	1.31	0.24	0.36	0.48	3.54	12.6	6.7
17	Guaranteed 2 per cent plus nitrogen	0.21	0.11	0.51	1.06	0.55	2.44	14.8	10 9
18	Guaranteed 2 per cent. plus nitrogen	0.81	0.98	0.09	0.43	0.48	2.79	13.2	6.9
19	Guaranteed 1 per cent. plus nitrogen	0.46	0.14	0.36	0.40	0.27	1.63	7.7	8.7
20	Guaranteed 1 per cent. plus nitrogen	....	0.63	0.18	0 29	0.31	1.41	11.9	5.1
21	Guaranteed 0.8 per cent. plus nitrogen	....	....	0.40	0.34	0.26	1.00	6.4	9.4
22	Guaranteed 0.8 per cent. plus nitrogen	....	0.21	0.27	0.37	0.40	1.25	15.8	4.9
	Mixtures of Known Composition								
23	50 Garbage tankage, 70 Ac. phos., 20 KCl	....	0.05	0.01	0.27	0.78	1.11	20.4	5.1
24	30 Garbage tankage, 10 Am. sul., 70 Ac. phos., 20 KCl	....	1.62	0.10	0.22	0.52	2.46	14.7	5.0
25	10 Blood, 70 Ac phos., 20 KCl	....	0.04	0.10	0.99	0.45	1.58	11.5	12.5
26	25 Blood, 70 Ac. phos., 20 KCl	....	0.04	0.10	2.12	0.86	3.12	22.1	13.4
27	26 Base (5 plus 3 blood (1)	....	0.22	0.87	1.19	0.70	2.98	22.1	8 6
28	26 Base (5) plus 3 H. G. tankage (2)	....	0.23	1.18	0.59	0.53	2.53	18.1	6.3
29	26 Base (5 plus 3 fish (3)	....	0.22	0.90	0.89	0.62	2.63	19.6	7.7
30	26 Base (5 plus 3 C. S. meal (6	....	0.22	0.94	0.61	0.55	2.32	18.2	6 4
31	26 Base (5 plus 3 med. tank (8)	....	0.25	0.97	0.49	0.46	2.17	16.6	5.7
32	26 Base (5 plus 3 garbage T. (12)	....	0.22	0.94	0.27	0.43	1.86	16.7	4.2
33	26 Base (5 plus 3 peat (13)	....	0.22	0.90	0.33	0.44	1.86	19.2	3.9
34	10 Dried blood, 5 C. S. M., 50 Ac. phos., 7 ½ KCl	....	0.03	0.04	1.75	0.68	2.50	19.3	12.6
35	20 Treated leather, 15 garbage tankage, 10 peat, 50 Ac. phos., 5 KCl	....	0.08	0 09	0 85	1 07	2.09	32.1	5 9

Similarly, the organic nitrogen in Nos. 17, 19 and 21 is of high availability, while that in Nos. 18, 20 and 22 is derived from inferior sources.

Mixtures of Known Composition, Nos. 23–35.

No. 23, "Inactive" far in excess of "active." A low grade material.

No. 24, "Inactive" far in excess of "active." A low grade material furnished the organic nitrogen. The total nitrogen availability of No. 24, owing to the presence of ammonium sulphate, is not questioned, but, nevertheless, the organic nitrogen in the mixture is low grade.

A laboratory method for nitrogen availability should not only differentiate between crude nitrogenous stock of high and low agricultural values, but must also make similar distinctions when the crude stock is incorporated into the ordinary mixed fertilizer. A comparison of the results under crude stock with those obtained in mixtures of known com-

position will show a very close agreement between "theoretical" and "actual" results. This indicates that "acid phosphate" and other ingredients are not "disturbing" factors and that the manufacturer having determined in advance the nitrogen activity of his crude stock may be assured of getting full credit for the nitrogen activity of his finished product.

ORGANIC AND VOLATILE MATTER.

A determination of the organic and volatile matter in the water insoluble portion of crude stock or a fertilizer will furnish a reliable clue to the character of the organic nitrogen in the material. The procedure in use at the Vermont Experiment Station laboratory is as follows: Weigh two grams of material onto a filter paper and wash with about 250 cc. of water at room temperature. Dry the residue at about 80° C. and transfer from the filter to a small tared porcelain dish (E. & A. 2963, No. 00). Place in an air bath and dry for 3 hours at 100° C. Cool in desiccator and weigh. Burn off organic and volatile matter over a Bunsen flame, stirring occasionally. Cool in desiccator and weigh. Calculate percentages of organic and volatile matter and ash.

The nitrogen in the washed residue (previously determined for the alkaline permanganate activity) multiplied by 100 and divided by the organic and volatile percentage gives the "per cent. nitrogen in the organic and volatile matter."

Reference to the last column in the table shows that this figure varies in crude stock from 4.0 to 16.9, the relatively high figures corresponding to materials of recognized high grade and the low figures to those classed as inferior for plant food purposes. Thus dried blood shows 16.3 "per cent. of nitrogen in organic and volatile matter," fish 11.7, cottonseed-meal 9.4, medium tankage 9.2, while garbage tankage contains 5.1, peat 4.2, and mora meal 4.6 per cent.

Applying this procedure to commercial fertilizers licensed in Vermont from 1908 to 1911, inclusive, a range from 4 to 13.6 per cent. has been found, the low figures without exception corresponding to low organic nitrogen activity.

The organic and volatile matter in different mixtures of acid phosphate and muriate of potash has been found to vary from 3 to 3½ per cent., but as only a comparative figure is wanted, we have thus far made no correction when using the method on commercial fertilizers.

Fertilizer.	Per cent. nitrogen in the organic and volatile matter.	Activity by alk. Permanganate method.	Fertilizer.	Per cent. nitrogen in the organic and volatile matter.	Activity by alk. Permanganate method.
1	12.0	65[1]	9	5.3	37
2	13.6	65[1]	10	5.2	33
3	11.8	73[1]	11	9.0	69[1]
4	4.0	39	12	9.1	68[1]
5	5.1	49	1499	11.6	83[1]
6	5.1	48	1546	9.6	73[1]
7	5.5	48	1560	8.9	74[1]
8	10.6	71[1]	1573	6.7	52

As yet, we have found no sample of crude stock or fertilizer that does not show the desired relationship between the percentage of "nitrogen in the organic and volatile matter" and activity of the water insoluble nitrogen, as measured by the alkaline permanganate method and vegetation tests. Thus, selecting at random from our results with commercial fertilizers collected during the past four years, the accompanying table indicates the general trend of results.

The point that the writer wishes to establish is that this determination of "nitrogen in the organic and volatile matter" will show whether the source of the water insoluble organic nitrogen is from materials rich in nitrogen or from those poor in this element.

[1] Nitrogen readily available for plant use.

VERMONT EXPERIMENT STATION,
BURLINGTON, VERMONT.

THE EFFECT OF THE "WET PROCESS" ON THE AVAILABILITY OF LOW GRADE NITROGENOUS MATERIALS.[1]

By BURT L. HARTWELL AND F. R. PEMBER.

Received January 12, 1912.

It has been known for a long time that the nitrogen in such materials as roasted leather, garbage tankage and peat is of very low availability, and for that reason the fertilizer laws of certain states do not permit their use in fertilizers.

The claim has been made, however, by certain manufacturers that the so-called wet process of treating such materials so completely changes their physical and chemical nature that their availability is materially increased; and that, after having been subjected to the wet process, they should not then be considered in the same class as the original materials, nor discriminated against in the same way. Although these claims seemed reasonable, those charged with the inspection of fertilizers could hardly accept them without experimental proof.

Largely through the influence of a certain manufacturer of fertilizers, a fertilizer works was finally thrown open in 1910 to a committee, consisting of C. H. Jones, chairman, J. P. Street and B. L. Hartwell, which had been appointed by the Directors of the agricultural experiment stations of the New England States, New York and New Jersey to investigate the subject of the determination, by laboratory methods, of the availability of organic nitrogen.

This committee witnessed the mixing of about a hundred tons of hair tankage, garbage tankage, roasted leather, phosphate rock and sulfuric acid, by the wet process, took samples of all materials used in the mixture, and securely sealed the "den" containing the manufactured material. Two days later, the chairman of the committee, who was present at the breaking of the seals and opening of the den, took samples of the finished product. The identity of the nitrogenous material had been practically destroyed by the treatment. The maximum thermometer placed near the bottom of the den had registered 208° F.

The following determinations made by C. H. Jones show some of the changes which took place in the nitrogenous material during the process.

[1] Presented at the American Chemical Society Meeting at Washington, D. C., December, 1911.

PER CENT OF TOTAL NITROGEN PRESENT IN DIFFERENT FORMS

	Before putting into the den	After removing from the den
In ammonium salts	6.5	14.3
In water soluble organic matter	7.8	57.7
In water insoluble organic matter	85.7	28.0

For vegetation experiments, the authors secured from the committee samples of the different nitrogenous materials which formed a part of the mixture, as well as of the final "base goods." Through the coöperation of Mr. Jones they were also supplied with similar low grade nitrogenous materials both in their unacidulated condition, and after they had been subjected individually to laboratory treatment with phosphate rock and sulfuric acid in a manner similar to that employed in the factory; in the case of each nitrogenous material, 500 grams of it were mixed with 750 grams of phosphate rock and 1250 grams of sulfuric acid.

Mr. Jones kindly furnished the following analyses of the material treated in the laboratory.

Per cent. of nitrogen in the material.

	Ammoniacal.	Water soluble organic.	Water insoluble organic.	Total.
Garbage tankage	0.02	0.23	2.61	2.86
Garbage tankage, acidulated	0.06	0.20	0.27	0.53
Treated leather	0.03	0.65	4.74	5.42
Treated leather, acidulated	0.04	0.78	0.16	0.98
Hair	0.28	0.60	10.77	11.65
Hair, acidulated	0.13	1.23	0.22	1.58

The nitrogen content of base goods made at the factory and of the identical materials which formed a part of the mixture, as finally used in the experiments, was as follows:

	Nitrogen. Per cent.
Hair tankage	6.28
Treated leather (roasted)	6.49
Garbage tankage	2.87
Base goods, including the above	1.68
Water soluble nitrogen in base goods	1.28
Water insoluble nitrogen in base goods	0.40

The materials which were treated with phosphate rock and sulfuric acid in the laboratory ("acidulated"), and those mixed in the factory, were of about the same grade with the exception of the hair goods. The hair tankage used at the factory was a mixture of hair, wool, etc., which had undergone some decomposition, with the formation of ammonia, whereas that treated in the laboratory was clean, fine hair, on account of this difference, both grades were included in the pot experiment.

The vegetation experiments were conducted in eight-inch Wagner pots. Natural soil from two different localities was used. Optimum amounts of lime, potassium, and phosphorus were provided in hydrated lime, sulfate of potash, Thomas phosphate and acid phosphate, in order that the differences in growth might be attributable only to differences in the availability of the nitrogen. Unless stated otherwise the same amount of nitrogen for each crop (0.1 gram) was added per pot in the different materials.

The results are given in the accompanying table.

GRAMS OF AIR-DRY CROPS GROWN SUCCESSIVELY WITH THE SAME AMOUNT OF NITROGEN, UNLESS OTHERWISE STATED, ADDED PER POT FOR EACH CROP

Source of nitrogen.	Grown in "Station" soil. Japanese millet	Oats	Buckwheat	Grown in "Larkin" soil. Oats	Japanese millet	Average relative increase in yield (Blood = 80)
None (check)	48.5	22.0	10.3	42.0	37.5	0
	50.0	23.5	9.3	48.5	35.5	
	49.5	24.0	8.0	44.0	35.5	
Hair tankage	53.0	30.5	14.5			
	49.5	32.0	11.3			59
Hair	48.5	28.0	11.0			
	49.5	30.0	11.5			33
Ditto, acidulated	55.5	31.0	12.5			
	52.0	31.0	11.0			64
Treated leather	51.0	25.5	12.5			
	50.5	24.0	10.5			23
Ditto, acidulated	56.0	33.0	16.5			
	56.0	29.0	10.0			80
Garbage tankage	48.0	22.5	10.5	48.0	40.0	
	48.0	24.5	9.5	46.0	41.5	13
Ditto, acidulated	49.0	22.0	8.5	50.5	34.0	
	48.5	21.5	10.0	54.0	34.5	8
Hair tankage, garbage tankage, and treated leather	48.0	29.5	11.0	54.0	43.0	
	47.0	29.5	10.3	56.0	44.0	49
Ditto, acidulated (base goods)	52.5	30.5	17.0	54.0	52.0	
	50.0	31.5	12.5	57.0	49.0	84
Insoluble part of base goods	43.5	22.0		44.0	36.0	
	48.0	20.6		46.0	43.0	0
Dried blood	50.5	33.0	12.0[1]	50.0	48.0	
	53.0	32.5	12.5	52.0	50.5	80
	52.0	30.0	21.0	54.5	49.0	
Ditto, with extra phosphorus	54.5	38.0[2]	26.5[2]	53.0	44.0	
	50.5	40.5[2]	26.0[2]	53.0	46.5	
Water soluble part of base goods	55.0	41.5[2]		53.0	51.0	
	58.7	40.0[2]		62.0	47.0	
Extra amt. blood	56.5	40.0	28.0	55.0	61.0	
	60.0	42.0	24.3	57.0	61.0	
Nitrate of soda	57.0	50.0[2]		61.0	49.0	
	56.5	46.5[2]		54.0	52.0	

In spite of the fact that an attempt was made to secure soils which were deficient in nitrogen, the first crop in the case of each soil proved to be nearly as large from the check pots, which received no nitrogen, as from the others. This is not an uncommon experience even with soils which have grown crops for some time without nitrogenous manures. It results from the fact that the application of lime, which proved necessary to maintain a soil reaction which was neutral to litmus paper and conducive to the utilization of organic nitrogen, led to the liberation of sufficient nitrogen to support a nearly maximum crop.

Although in the case of both soils, for the reason stated previously, distinct differences did not result from the different applications, it was decided nevertheless to include the results with those secured with the subsequent crops grown in the same soils after renewing the manurial applications including the nitrogenous materials.

The different nitrogenous substances, therefore, not only had an opportunity to exert their effect upon the crop immediately following their application,

[1] Omitted from the average.

[2] Received the same amount of nitrogen as was in the extra amt. of blood.

but also their after-effect upon one or two succeeding crops.

In the last column of the table is given the relative availability of the nitrogen in the different materials, arbitrarily considering 80 as the availability of the nitrogen of the dried blood (13.62 per cent. nitrogen), and deriving the availability of the nitrogen in the other materials from the increase in growth in each case over the appropriate check crops as compared with the increase caused by the dried blood. It is evident that only such of these values as are based upon results with the same number of crops should be strictly compared.

The comparisons which should be emphasized in this connection are those concerning the availability of the nitrogen in the materials before and after being "acidulated," or subjected to the wet process.

It may be seen that although the availability of the nitrogen is 33 in the unacidulated hair and 23 in the treated leather, the availabilities are increased to 64 and 80, respectively, in the same material after being subjected to the wet process in the laboratory. The nitrogen in the garbage tankage, however, had a very low availability both before and after treatment. When the identical hair tankage, garbage tankage and treated leather, which were used in the fertilizer factory for the manufacture of the base goods, were applied to the pots in the same proportions as used in the works, the availability of the nitrogen was 49, whereas that in the base goods made from the same materials was 84.

About 90 per cent. of the nitrogen in the various unacidulated materials was insoluble in water, and although a half of the total nitrogen in the garbage tankage was still insoluble after acidulation, only about a fifth of the nitrogen in the acidulated roasted leather and hair tankage remained insoluble.

That part of the nitrogen of the base goods which was rendered soluble by the wet process seems to have had an availability higher than that in blood, whereas the insoluble nitrogen was practically useless.

Vegetation experiments to determine the availability of the nitrogen in such material as base goods, containing large amounts of available phosphorus, have to be conducted with every possible precaution to prevent the results being influenced by the phosphorus. The details of the consideration given to this matter in the present instance would be out of place in this brief paper. The principle was followed of supplying phosphorus so liberally that more would be without influence on the crops. It may be seen by reference to the table that when an extra amount of phosphorus was furnished in addition to the application of the dried blood, which served as a standard, no increase of crops resulted. Nevertheless, it is best to be conservative in comparing the nitrogen availability of highly nitrogenous non-phosphatic materials, like hair, leather and blood, with the same materials when existing in a mixture with a nitrogen content of less than 2 per cent. and with a high content of phosphorus. Furthermore, when such comparatively small differences as exist in experiments of this kind between the weights of the crops from the check and from the dried-blood pots are divided into 80 parts, it is evident that the "limit of error" is wide, and that certainly a difference of less than 10 in availability is of very little significance.

In view of these considerations, the claim is not made, therefore, that the nitrogen in acidulated leather and base goods is as valuable as that in dried blood. It is believed, however, that the experiments prove the efficiency of the wet process, when properly carried out, for materially increasing the availability of certain low-grade nitrogenous materials.

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KINGSTON, R. I.

NEUTRAL AMMONIUM CITRATE SOLUTION.[1]

By A. J. PATTEN AND C. S. ROBINSON.

Received January 12, 1912.

Since the proposal of the ammonium citrate method for the determination of available phosphoric acid, much trouble has been experienced in preparing a strictly neutral solution of the reagent. The weakness of both the acid and the base renders the end point quite indistinct with ordinary indicators, and much time and patience are required on the part of the operator to obtain the desired results. Several modifications of the simple titration method have been proposed, but each has objections which prohibit its common acceptation by practical chemists. The importance which the method has assumed in agricultural work demands, however, that some convenient means be devised for preparing the necessary solution. Such a method has recently been proposed by Hall and Bell[2] and was later shown by Hall[3] to be quite suitable for laboratory use. At the time these articles appeared, the authors of this paper were engaged in working out the same method, and the results are here offered, not with the hope of claiming the credit for originating the method, but simply as corroborative evidence in favor of its general adoption.

Of the several methods proposed as substitutes for the present official method, that recently suggested by Hand,[4] using purified litmus solution or azolitmin, seems to be the most promising. In order to test it out and compare it with the official corallin method as well as to obtain some data as to the accuracy of the latter an acid solution of ammonium citrate was made up and neutralized by these two methods by each of four analysts working independently.

An acid citrate solution was chosen of which 50 cc. required 7.50 cc. of the dilute ammonia solution for neutralization as determined by the conductivity method to be described later. The dilute ammonium hydroxide solution (about 3 per cent.) was kept in a burette enclosed in opaque paper to prevent the reading being taken until the supposed neutral point had been reached. In this way each operation was made independently of the others. Great care was taken that no loss of ammonium hydroxide should occur

[1] Presented at the American Chemical Society Meeting at Washington, D. C., December, 1911.

[2] *Jour. Am. Chem. Soc.*, **33**, 711 (1911).

[3] THIS JOURNAL, **3**, 559 (1911).

[4] U. S. Dept. of Agric., Bur. of Chem., *Bull.* **132**, p. 11.

during the process. The results are given in Tables I and II.

TABLE I.

With coralin as the indicator.

Cubic centimeters dil. NH_4OH		Cubic centimeters dil. NH_4OH	
Number.	Per 50 cc. sol.	Number.	Per 50 cc. sol.
P I	12.30	M I	16.00
P II	12.10	M II	15.00
P III	16.20	M III	16.40
P IV	12.70	M IV	16.60
R I	12.00	I I	12.20
R II	12.00	I II	13.60
R III	14.30	I III	19.60
R IV	13.60	I IV	15.90

TABLE II.

With purified litmus as the indicator.

Cubic centimeters dil. NH_4OH.		Cubic centimeters dil. NH_4OH.	
Number.	Per 50 cc. sol.	Number.	Per 50 cc. sol.
P I	15.00	M I	14.00
P II	13.76	M II	15.00
P III	16.00	M III	12.50
R I	15.00	I I	15.82
R II	17.50	I II	15.82
R III	14.00	I III	15.00

An inspection of these results reveals the fact that the Official Method gives extremely inconsistent results even in the hands of one person. In only one case was an exactly neutral solution secured. The variation in the results obtained by one analyst using this method amounted to seventy-four cc. of the dilute ammonium hydroxide solution per liter of the acid citrate solution. While this is the maximum variation in the four sets of determinations given, it must, nevertheless be accepted as a possibility in actual practice. Such a condition is surely anything but deirable and demands immediate attention. The other method showed to much better advantage. Not only were the results more consistent, but one-third of the trials actually gave neutral solutions.

These examples fairly illustrate the difficulty in making an exactly neutral reagent by the methods most in use, and it is quite possible that in many cases the character of the "neutral" ammonium citrate solution varies more than in the cases cited and that considerable error may be introduced into determinations in this way. It is evident that not only is there a wide variation in the solutions made by different individuals, but that even the same person can rarely duplicate his own results.

It has long been realized that it was impossible to get consistent results in neutralizing ammonium citrate solution by the Official Method, but it has been assumed that the differences in the acidity of the solution were too small to cause any appreciable error in the determinations made with them.

In order to test the correctness of this assumption, several actual determinations were made. The solutions used were R II, C,[1] M IV, and I III. They were carefully diluted to a specific gravity of 1.09 and the determinations were all made at one time so that there could be no variation due to temperature of the bath. Determinations were made on two samples of fertilizer, one containing a small percentage of insoluble P_2O_5 and the other a large percentage. The results are given in Table III:

[1] Neutralized by the conductivity method.

TABLE III.

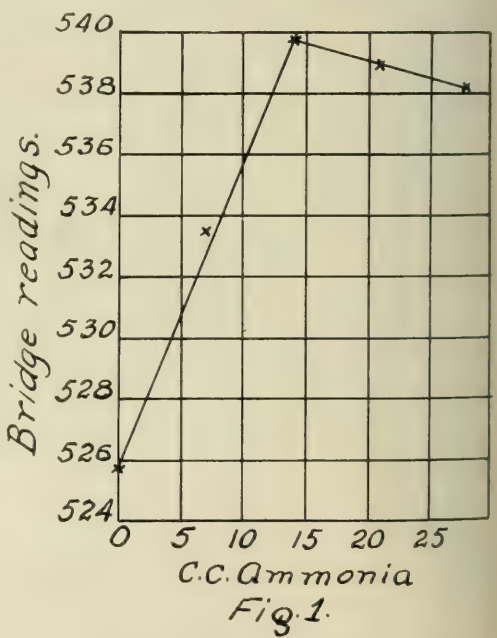
	cc. dil. NH_4OH	Sample I.		Sample II.	
Number.	Per 50 cc. sol.	Insol. P_2O_5. Per cent.	Average.	Insol. P_2O_5. Per cent	Average.
		2.84		8.86	
R II	6.00	2.81	2.83		8.84
		2.83		8.82	
		3.54		9.82	
C	7.50	3.80	3.69		9.81
		3.74		9.80	
		4.23		10.10	
M IV	8.30	4.07	4.17		10.04
		4.21		9.98	
		4.79		10.56	
I III	9.80	4.77	4.82		10.46
		4.90		10.36	

An inspection of these results shows a marked relationship between the reaction of the ammonium citrate solution and the amount of phosphorus pentoxide extracted.

These variations, amounting to 1.99 per cent. in one case and 1.62 per cent. in the other, are certainly significant. The results prove that perfect neutrality of the citrate solution is of the utmost importance in securing consistent results, as the above differences are of sufficient magnitude to make the method extremely uncertain.

CONDUCTIVITY METHOD.

The above-mentioned method, proposed by Hall and Bell, was found to be much more satisfactory. It depends upon the fact that when different quan-



tities of alkali are added to an acid solution (or *vice versa*) the electrical conductivity or resistance of the

solution will vary with each addition, and if these resistances or conductivities are plotted against the amounts of alkali or acid added, there is a sharp change in the direction of the curve at the neutral

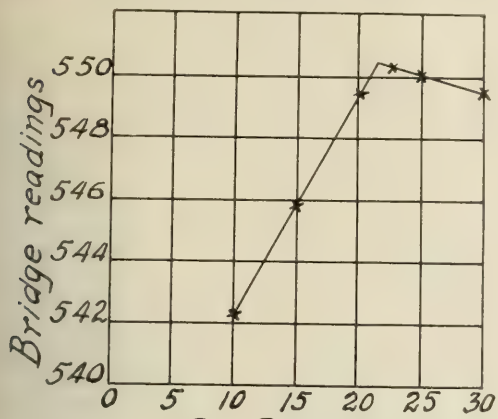


Fig. 2.

point. This property has been made use of for the titration of various liquids where color changes were difficult to observe and has given very good results.

The method of procedure as given by Hall is quite satisfactory. A solution of citric acid is almost neutralized, the density being kept above 1.09. Small samples of this solution are then titrated with a dilute solution of ammonium hydroxide, using corallin as an indicator, to determine the approximate amount required to neutralize the remaining acid. Definite quantities of the citrate solutions are removed with a pipette and transferred to clean, dry, volumetric flasks. To these portions of the original solution varying quantities of the dilute ammonium hydroxide are added in such a way that some of the flasks contain more and some less than the approximate amount required for exact neutralization as determined by the titration with corallin. These solutions are then made up to the same volume with distilled water, placed in a thermostat, the temperature of which is held constant, and allowed to come to the temperature of the bath after which their resistances are measured by the Wheatstone bridge method. Plotting the cubic centimeters of ammonium hydroxide against the bridge readings gives a curve from which may be read the exact amount of ammonium hydroxide required to neutralize the acid in a given quantity of the citrate solution.

The following are some of the results obtained and illustrate the sharpness with which the neutral point may be read:

TABLE IV.

No.	Cc. dil. NH_4OH per 50 cc. sol.	Bridge readings.	No.	Cc. dil. NH_4OH per 50 cc. sol.	Bridge readings.
1	0.0	525.75	4	21.0	539.00
2	7.0	533.50	5	28.0	538.25
3	14.0	539.75	6	35.0	537.25
			Neut.	14.0	539.75

No.	Cc. dil. NH_4OH per 100 cc. sol.	Bridge readings.	No.	Cc. dil. NH_4OH per 100 cc. sol.	Bridge readings.
1	10.0	542.25	4	22.5	550.25
2	15.0	545.75	5	25.0	550.00
3	20.0	549.50	6	30.0	549.50
			Neut.	21.6	550.35

ACCURACY OF METHOD.

In order to test the accuracy with which results may be duplicated by different operators, a stock solution of acid ammonium citrate was made up and neutralized independently by four laboratory assistants, three of whom had never before made any conductivity measurements. One hundred cubic centimeter portions of the acid solution were transferred to 250 cc. volumetric flasks, the designated amounts of ammonium hydroxide added, and the bridge readings taken. Each operator made four sets of determinations on the same solution, the conditions being altered each time so as to give different readings for each set, thus eliminating any error due to the operator attempting, unconsciously or otherwise, to duplicate his previous results. Each one was required to plot his own results and report independently the amounts of ammonium hydroxide required to neutralize the acid in the quantity of citrate solution taken. The results are given in the following table:

TABLE V.

No.	Cc. dil. NH_4OH per 100 cc. sol.	No.	Cc. dil. NH_4OH per 100 cc. sol.
P I	13.80	M I	13.50
P II	13.60	M II	14.20
P III	13.80	M III	13.00
P IV	13.80	M IV	13.90
R I	14.00	I I	13.50
R II	13.50	I II	13.00
R III	13.00	I III	13.60
R IV	13.90	I IV	13.20

For the sake of comparison, averages of the several determinations made by each method are given in Table VI:

TABLE VI.

Average of	Corallin method.	Litmus method.	Conductivity method.
P series	13.32	14.92	13.75
R series	12.98	15.50	13.60
M series	16.00	13.84	13.65
I series	15.32	15.54	13.32
Av. of all series	14.41	14.95	13.58
Maximum variation	3.02	1.70	0.43
Maximum variation	+1.59	+0.59	+0.17
Above (+) and below (−) average	−1.43	−1.11	−0.26

The determinations by the corallin and litmus methods were made on the same solution, but the determinations by the conductivity method were made upon a solution of slightly different strength. The advantages of the conductivity method over the other two is well illustrated in the above table. The results by the corallin and litmus methods are very variable, the greatest variation in the first case being 3.02 while in the second maximum variation is 1.70. The results by the conductivity method are very much closer, the maximum variation in the averages being only 0.43. If we assume the average of all the

series by this method, to be the true result, then the maximum variation below this result is only 0.17 and the maximum variation above is 0.26.

These differences might well be considered within experimental error.

RATIO OF AMMONIA TO CITRIC ACID.

Dr. McCandless, the referee on phosphoric acid for the Association of Official Agricultural Chemists, in 1909, suggested that a reagent be used which should have the same ratio of ammonia to citric acid as the pure triammonium salt. This ratio is 1 : 3.765. He made some coöperative tests with three other chemists, in which solutions were obtained having ratios from 1 : 3.775 to 1 : 4.189. Some time later the Division of Fertilizer Chemists of the American Chemical Society recommended a solution in which the ratio of ammonia to citric acid was 1 : 4.25. A neutral solution was made up by the conductivity method and the ratio of ammonia to citric acid determined. An average of three determinations gave a ratio of 1 : 3.785. This would probably have approached still closer to the theoretical ratio if the neutral solution had been made up immediately after making the conductivity measurements. During the several days that elapsed between the determinations of the quantity of dilute ammonium hydroxide solution required to give perfect neutrality and the actual preparation of the neutral solution, the strength of the dilute ammonium hydroxide solution was probably changed. It seems probable that this method could be used to give more satisfactory results than the present Official Method.

CONCLUSIONS.

The present Official Method for preparing a neutral solution of ammonium citrate is extremely unreliable.

The purified litmus method gives somewhat better results, although the limit of error is too great for reliable work.

The conductivity method, on the other hand, is reliable and not difficult of operation and the results obtained by different workers agree very closely.

LABORATORY AND PLANT

THE MANUFACTURE OF GELATINE.[1]

By Ludwig A Thiele.

Received Dec. 22, 1911.

INTRODUCTION.

The manufacture of gelatine, originating in the remote past, when jelly was produced by boiling calves' feet in the kitchen, with the most crude and primitive methods, has now arrived at such a state of perfection, through the application of chemical as well as engineering science, that this industry may justly be proud of its progress.

To-day gelatine is manufactured in millions of pounds, and plays a great role in the nutrition of the people.

While the bulk of gelatine is manufactured for edible purposes—for jellies, jams, for the candy industry and for ice cream, which product comes under the Pure Food Law—the gelatine used in the arts, for photographic dry plates and papers, for medical purposes in the form of capsules, for bacteriological purposes and for decoration of fancy goods, does not come under this law; nevertheless, all these varieties are made practically the same, with like care and precaution, from the most select raw materials, and under the most sanitary conditions which may be applied to such an industry.

The manufacture of gelatine comprises the following distinct operations:

I. Treating and cleaning the raw material.
II. Dissolving the gelatine.
III. Concentrating the gelatine solution.
IV. Chilling and spreading.
V. Drying.
VI. Finishing (grinding and packing).

The most important raw material consists of:

a. Bones (osseine), hornpiths and button bones.

b. Hidestock (calf-pates, trimmings and fleshings).

(*a*) Osseine is the organic substance contained in the bones, the manufacture of which originates from France.

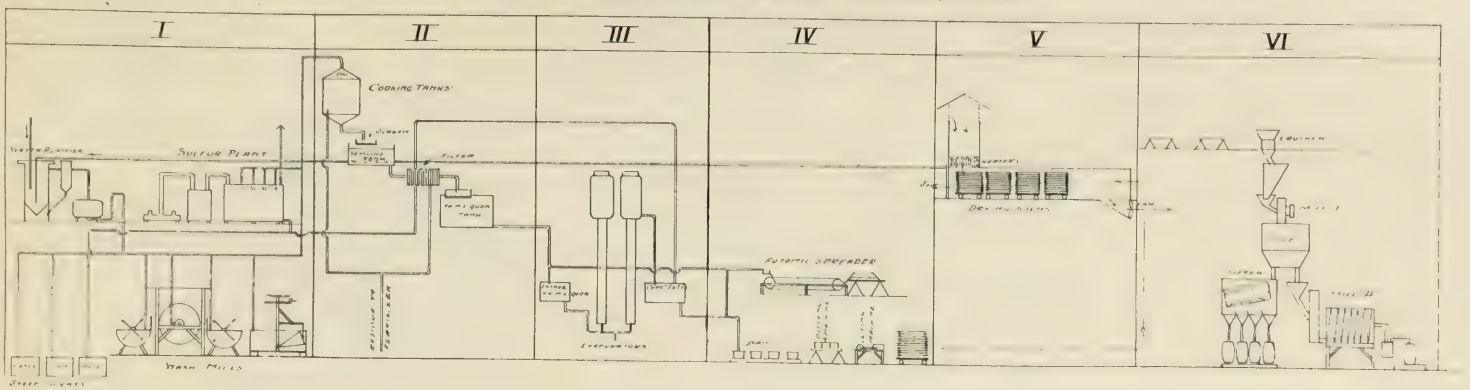
Raw bones are not used in the manufacture of gelatine at all, but have to undergo a preliminary treatment in order to produce osseine. The treatment for osseine and hidestock is then practically the same. Let us therefore first consider the preliminary treatment of the bones.

Bones, as obtained either direct from the slaughterhouses in raw and wet state, or in dried form through dealers, have to be washed, crushed and degreased in special extraction plants by means of benzine or carbon tetrachloride. In this stage of manufacture, from 8 to 10 per cent. of bone fat is produced from the bones, while the water contained in the raw bones is nearly eliminated. The crushed, degreased bones now undergo the same treatment as the East India crushed bones, which contain practically no fat, by extracting the mineral substance by means of diluted acids. This process, called maceration, produces about 60 per cent. of acid phosphate, a very valuable by-product. The acids to be used in the manufacture of osseine are either hydrochloric, phosphoric or sulphurous, or, according to the process of Bergmann, hydrochloric combined with sulphurous acid. Until quite recently, the drawbacks attending the use of sulphurous acid prevented its application in the extraction of osseine from bones. In order to prevent the surface of the bones from becoming coated with a layer of tribasic calcium phosphate, it was necessary to keep either the liquid or the bones in constant motion.

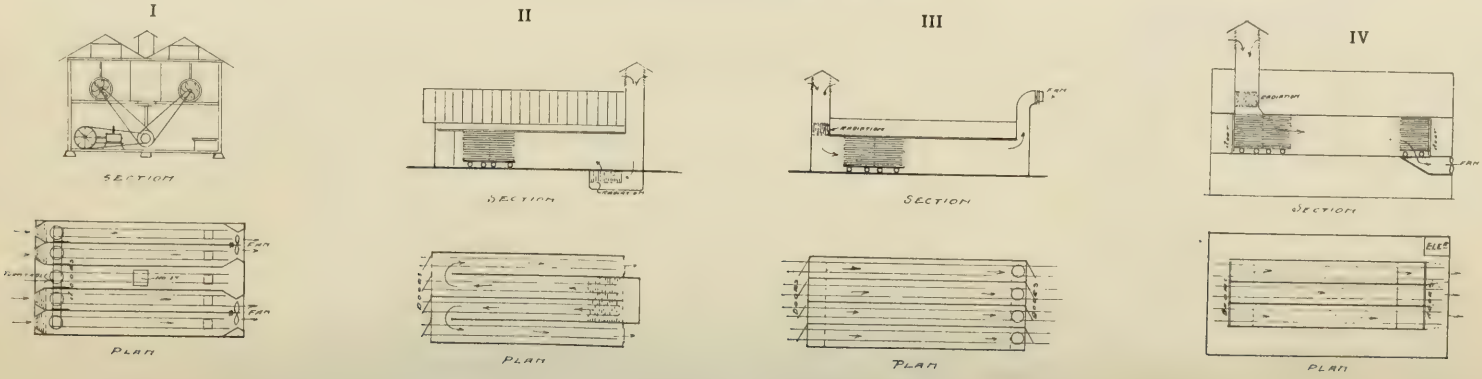
In the *Bergmann process* these difficulties are obviated by causing the solution of sulphur dioxide to circulate through a battery of closed tanks in which the bones are treated, the solution being continually

[1] Presented at the Fourth Annual Meeting of the American Institute of Chemical Engineers, Washington, Dec. 22, 1911.

DIAGRAM SHOWING MANUFACTURE OF GELATINE BY LUDWIG A. THIELE.



PLANS OF DRYING KILNS. BY LUDWIG A. THIELE.



enriched by sulphur dioxide as it is neutralized by the calcium phosphate. After having gone through four tanks the solution is still sufficiently acid to retain in solution the whole of the extracted phosphate. The resulting saline liquid is a solution of monobasic calcium phosphate in calcium bisulphite solution. In order to separate the calcium phosphate in the form of dibasic calcium phosphate, and to recover the sulphur dioxide, this liquid is heated by means of steam in a lead-lined autoclave, termed "The Digester." This reaction liberates from the calcium bisulphite its sulphur dioxide, which is then conducted back to the acid tanks. At the same time one equivalent of the calcium bisulphite reacts with the monobasic calcium phosphate to form dibasic calcium phosphate, which falls to the bottom of the boiling liquid and normal calcium sulphite. In order to decompose the latter, an exactly measured quantity of hydrochloric acid is introduced into the Digester. The liberated sulphur dioxide is returned to the acid tanks, while the aqueous liquid containing calcium chloride in solution and dibasic calcium phosphate in suspension, is withdrawn, decanted, and filtered, and the separated phosphate drained on a porous surface and dried. The inventor claims that the so obtained dibasic calcium phosphate is white and pure, and completely soluble in ammonium citrate solution, which is not the case when the phosphates are separated by other methods. The loss of sulphur dioxide in a well managed factory is said not to exceed 5 per cent. of the weight of the bones. The osseine thus freed from phosphate appears to be whiter and of better quality than that obtained by the use of hydrochloric acid entirely, which renders the osseine yellow and makes the preparation of colorless gelatine more difficult.

(*b*) Hidestock is received in green, salted, limed or dried form at the factory.

Another important feature in the manufacture of gelatine is the water, which should be soft, nearly free from lime-magnesia-carbonates or sulphates, and free from iron.

I. From this stage, the process of manufacture of gelatine from osseine, as well as hidestock, is practically the same, and the material passes into the first stage of manufacture. The animal matter is introduced into steeping vats, in which it undergoes the process of washing, a treatment with lime or caustic soda in order to saponify the last traces of fat and to swell the material. After liming follows another operation of washing, followed by an acid bath to destroy the alkali and bleach the raw stock. From the steeping vats the thus prepared raw material passes into the wash mills to be washed perfectly neutral. It is absolutely necessary to observe these preliminary stages of manufacture very carefully, as traces of acids or other impurities contained in same may discolor the gelatine produced.

There are several distinct types of wash mills, of which the following may be mentioned:

1. Half-round mills of about 6′ wide, 12′ long and 42″ deep, provided with perforated false bottoms and eccentrically arranged paddles.

2. Revolving Circular Mills into which water is injected by means of a hollow perforated shaft passing through the center of the mill. Both these types are mainly used for washing osseine and material of finer structure.

3. For washing calf-pates or hidestock, the so-called Roller Wash Mill is generally used, which consists of a circular tank, 16′ in diameter and about 40″ high, in which revolves a cone-shaped roller.

The average speed of these wash mills ranges between 14 to 20 revolutions a minute. After the raw material is thus prepared, it enters into the second stage of operation.

II. Extraction tanks are generally about 6′ in diameter and 5′ high, provided with false bottoms and with perforated circulation chimney arranged in the center. The extraction tanks are provided with steam coils below the false bottom, and sometimes surrounding the tank.

There are also steam-jacketed tanks, which otherwise are practically of the same construction. The raw material is rinsed from the wash mills, having absorbed about three and one-half times its original weight of water. It is then conveyed to the extraction tanks, covered with warm water, steam turned on, and the thin gelatine solutions are continually drawn off, as soon as they contain from 4 to 6 per cent. of gelatine. There are produced from 4 to 8 subsequent "runs," the temperature of which varies with the different factories and the process applied, ranging from 130–200° F. The charge of one extraction tank being about 2000 pounds of dry raw material, containing about 60 per cent. of gelatine, will result in producing from 3000–4000 gallons of thin gelatine solution. By the usual process of extraction making different consecutive "runs," these are all of different densities and the process is comparatively slow. Therefore, many manufacturers, anxious to find a process to produce the gelatine solution in a continual run, patented processes of continual extraction which the following may exemplify.

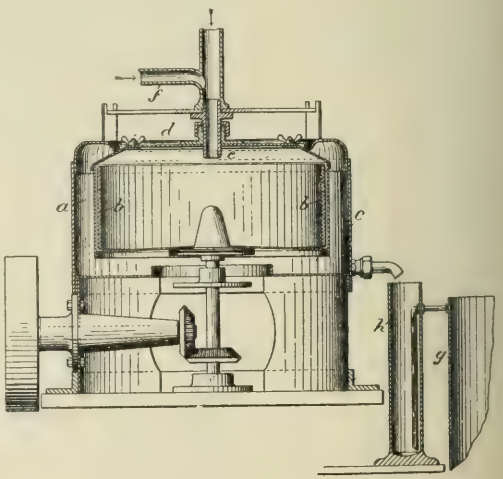


Fig. 1.—Cormack's Extraction Apparatus.

In 1903 *Cormack* obtained U. S. patent No. 728,205 for a process under centrifugal force, consisting in washing the gelatinous material, cutting it up, and subjecting it in this divided state to the simultaneous action of condensing steam and centrifugal force, dissolving the gelatine out of the material, passing the solution from the material by gravity and centrifugal force, and thereby filtering, collecting, and finally drawing off the solution.

In 1910, *Lehmann*, Paris, obtained U. S. P. No. 964,980, describing the combination in a gelatine manufacturing apparatus, of a casing for the reception of liquid, means for heating the liquid, and rotable drum composed of perforated material located in

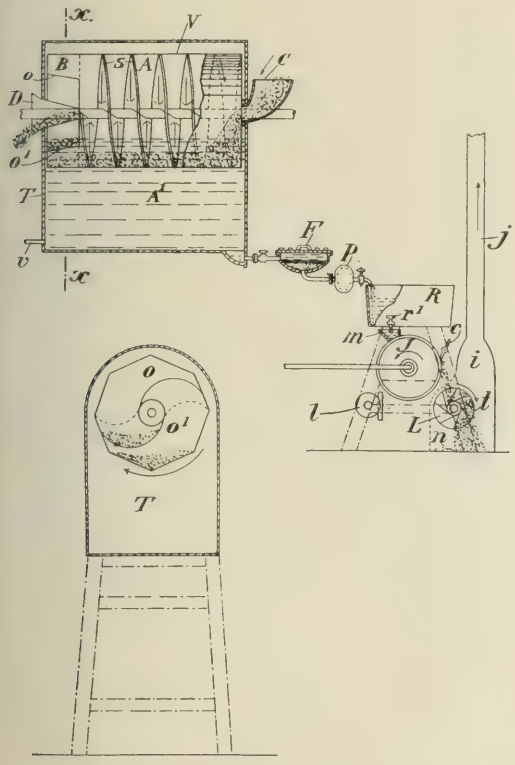


Fig. 2.—Lehmann's Extraction Process.

said casing, means for feeding the material to be operated on into said drum, a screw in said drum consisting of a shaft and rotary curved blades mounted on the shaft for the purpose of discharging the insoluble materials from the drum, a conical outlet pipe in said casing, means for clarifying the extracted gelatinous solution comprising a filter, a rotary pump and a grease reservoir, means for desiccating the clarified solution comprising a hopper under said grease chamber, and a rotary heated drying cylinder mounted beneath said hopper, a blade in contact with the cylinder mounted beneath said blade, and means for hastening the cooling of the finished product.

In 1911, *Thiele* obtained U. S. P. No. 989,826, an appliance for reducing animal matter to gelatine, a steam-tight tank, and inner perforated cage, a steam coil between the tank and cage, a steam heater, a water pipe passing through said heater, and into the tank, a spraying device on said pipe within the tank,

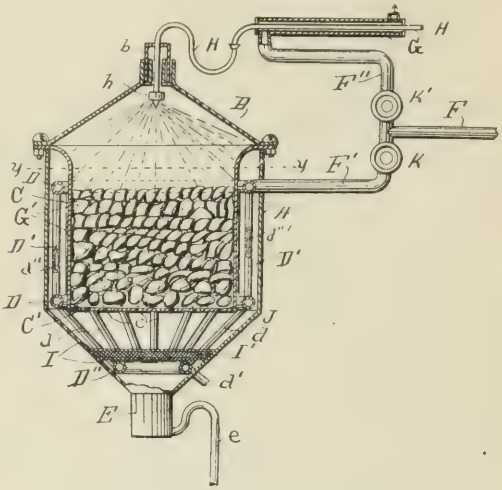


Fig. 3.—Thiele's Extraction Apparatus.

a steam pipe leading to the steam coil and to the steam heater, shut-off valves in the steam pipe between the steam heater on one side and the steam coil on the other side, a settling chamber including a filtering device below the cage, a receptacle below the filtering device for receiving the filtered substance from the cage, and a siphon for drawing off the contents of the receptacle.

This latter device, arranged in pairs, enables continual operation, producing but one grade of gelatine from the entire batch. In case the production of different qualities is required, the thin gelatine liquors should be divided according to the time of efflux. Neither of the extraction processes produce gelatine liquors which are exactly clear. They should be screened into a settling tank, from which these thin gelatine solutions pass through a filtering device. Some efficient filters for gelatine are the Karl-Kiefer filter, the Union Schalen filter, or the International filter. Filtering paper or paper asbestos pulp is generally used in these constructions.

Utley, in U. S. P. No. 961,180, describes a charcoal filter which, besides giving a brilliant filtrate, claims to eliminate discoloration.

In some cases the last extracted portions or runs of gelatine are very cloudy and the filters before described are not in state to render the filtrate of great brilliancy. In such cases these runs should be clarified, either by the alum-phosphoric-acid, blood albumen-SO_2 or egg albumen processes. The only drawback to these chemical clarifications is that the gelatine solutions are weakened, and in some other processes there remains a soapy odor, with a tendency to foam and quicker putrefaction. The clarified thin gelatine solutions are usually kept in storage tanks for 6–8 hours, giving time to settle. Usually a very slight precipitation occurs in these

solutions. These purified gelatine solutions now pass into the third stage of manufacture.

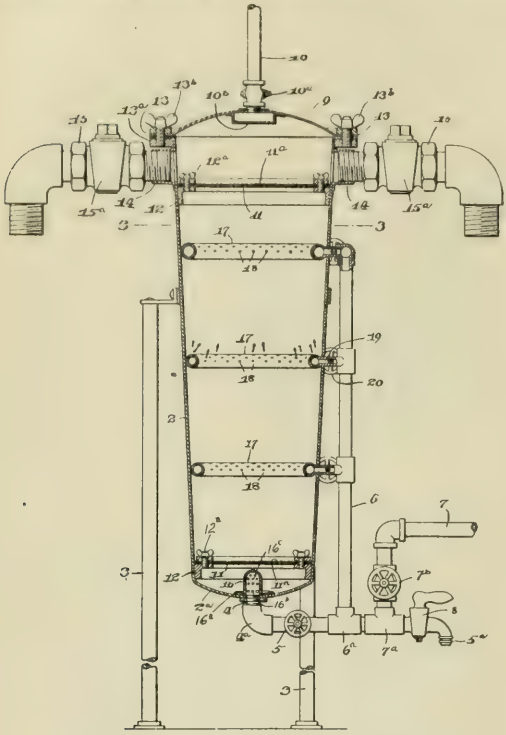


FIG. 4.—UTLEY'S FILTERING APPARATUS.

III. The concentration of the thin gelatine solutions is usually made by evaporators. Concentration in open pans is probably entirely eliminated by this time. Single, double and triple effects are used as evaporators, depending on the size of the factory and the quality of gelatine to be produced. Very common systems of evaporators are those of Yaryan, Swenson, Zaremba, and Kestner.

The thin gelatine solutions are concentrated in the evaporators from 4–6 per cent. to 10–20 per cent., depending on the quality of gelatine to be produced. If it is the object of the factory to produce gelatine in thin sheets, it is not advisable to concentrate the thin solutions too strong, but rather to draw off the solutions at from 5–6 per cent. and chill them direct. It is a difficult matter to spread these jellies containing but 4–6 per cent. of dry gelatine by hand. This drawback caused many attempts, which date back as early as 1870, to construct apparatus which would eliminate spreading by hand.

Following are some patents obtained on apparatus of this nature:

1870, Andrew Dietz, New York, U. S. P. No. 103,852; 1870, Wm. Adamson, Philadelphia, U. S. P. No. 106,448; 1877, Chas. O. Garrison, New York, U. S. P. No. 185,825; 1878, E. W. Leggett, Elizabethport, U. S. P. No. 205,968; 1886, King Upton, Salem, Mass., U. S. P. No. 338,374; 1886, Wm. P. Upham, Melrose, Mass., U. S. P. No. 343,507; 1888, Chas. Keller, Springdale, Pa., U. S. P. No. 386,590; 1893, F. A. Wolff, Heilbronn, Germany, U. S. P. No. 496,469; 1894, Peter Cooper Hewitt, New York, U. S. P. No. 521,371; 1894, Chas. W. Cooper, New York, U. S. P. No. 521,947; 1899, Schill & Seilacher, Stuttgart, Germany, D. R. P. No. 119,477; 1907, O. Koepff, Goeppingen, Germany, Aust. P. 33,510.

At the present time the constructions of *Wolff, Hewitt, Schill & Seilacher, Koepff, and Clyde* are in use. These mechanical spreading devices are used only where the gelatine is to be manufactured in thin slices or sheets, to be later sold in packages, or for the shredded qualities. In most cases these apparatus consist of rotary drums or endless belts upon which the solution is run, and by cooling devices chilled, scraped off, and directly laid on the nettings. By nettings is understood a frame 6′ × 3′ upon which is stretched a cotton or wire netting. After evaporation the material enters into the fourth stage of manufacture.

IV. If no automatic spreader is used, the thin, concentrated evaporated gelatine solutions are drawn off into moulds. The moulds are usually pans 36″ long, 5″ deep, 9″ wide at the top and 8″ wide at the bottom, giving them a tapering form in order to allow the jelly to be easily turned out. These jelly blocks are then separated into smaller blocks by means of a blocking machine, which are again made into thin slices by means of a slicing machine. The slices are then laid on the nettings by automatic machines or by hand and the nettings subsequently piled one upon another, about 1½″ apart for the purpose of circulation, to a height of twenty-five or thirty racks upon a car or truck, and now pass into the fifth stage of manufacture.

V. In the sketches on p. 447 are shown four distinct types of drying processes.

The drying of the gelatine is conducted in channels or kilns, which are provided with rails for the easier handling of the trucks. These alleys have a total length of from 70 to 100 feet, by 6′ 6″ square, are provided with heating coils at one end and exhaust fans at the other, or with blowers arranged before the heaters, a continuous current of air being blown or drawn through the channels, while the cars conveying the gelatine slices are passed through the channels in the opposite direction. The material difference between the use of blowers or exhaust fans is the difference in H. P. required to run them. The drying process is carried on at a temperature varying from 85° to 105° F. This process is a most important one, as an inefficient circulation of saturated air in the kilns will produce moldy goods, a too strong current of air will warp the sheets, a too slow current will cause the gelatine to adhere too strongly to the nettings, while too great heat will cause the gelatine to turn liquid and run through the nets; therefore, the design of the drying plant should have the most careful consideration, as the following explanation of the drying theory may illustrate.

The process of desiccation by means of heated air rests entirely upon its avidity for humidity, but the capacity of absorption varies enormously with increased temperature. At 0° F. the absorption is very low, at 152° F. considerable, while at 212° F. it is infinite. If the air, for example, contains a certain quantity of vapor, it is said this vapor has a certain elastic force, which is expressed in inches of mercury. When air is charged with all the humidity

it can carry, it is said to be saturated. The following table gives the data of the elastic force of vapor in saturated air at temperatures ranging from zero to 212° F.

The weight in pounds of the vapor mixed with 100 pounds of pure air at any given temperature and pressure is given by the formula

$$\frac{62.3 \times E}{29.92 - E} \times \frac{29.92}{p},$$

where E equals elastic force of the vapor at the given temperature in inches of mercury, p equals absolute pressure in inches of Mercury = 29.92 for ordinary atmospheric pressure.

Temperature.		Elastic force of vapor.	Weight of vapor		Weight of vapor mixed with 1 lb. of air.
		Inches M/M Mercury.	Pounds per cu. ft.	Gram per cu m.	
° F.	° C.				
0	—17.8	0.044	0.11	0.000079	1.25	0.00092
12	—11.1	0.074	0.18	0.000130	2.08	0.00155
22	— 5.6	0.118	0.30	0.000202	3.22	0.00245
32	± 0	0.181	0.46	0.000304	4 86	0.00379
42	— 5.6	0.267	0.67	0.000440	7.04	0.00561
52	11.1	0.388	0.98	0.000627	10.01	0.00819
62	16.7	0.556	1.41	0.000881	14.08	0.01179
72	22.2	0.785	1.99	0 001221	19.53	0.01680
82	27.8	1.092	2.77	0.001667	26.68	0.02361
92	33.3	1 501	3.81	0.002250	36.02	0.03289
102	38.9	2.036	5.17	0.002997	47.96	0.04547
112	44.4	2.731	7.63	0.003946	63.16	0.06253
122	50.0	3.621	9.20	0.005142	82.31	0.08584
132	55.6	4.752	12.11	0.006639	106.22	0.11771
142	61.1	6.205	17.90	0.008473	235.65	0.16170
152	66.7	7.930	20.14	0.010716	171.56	0.22465
162	72.2	10.099	27.91	0.013415	214.76	0.31713
172	77.8	12.758	32.58	0.016682	266.91	0.46338
182	83.3	15.960	40.53	0.020536	328.78	0.71300
192	88 9	19.828	50.54	0.025412	402.52	1.22643
202	94.4	24.450	62.10	0.030545	488.79	2.80230
212	100.0	29.921	76.00	0.036820	589.49	Infinite

The above table shows that the capacity of air for water is not in proportion to the temperature, but progressive. The degree of saturation or relative humidity of the air is determined by the use of the dry and wet bulb thermometer (pychrometer) which instrument necessitates the use of hygrometric tables.

A very handy device for the determination of the humidity in air is manufactured by the Taylor Instrument Company under the name of "Hygrodeik." In order to get the most satisfactory results in drying, it is necessary to make the aforesaid observations in the ingoing and outgoing air, as well as to determine the velocity of the air current by means of an anemometer.

In the process of drying there will also be observed that (1) the more concentrated a solution, the longer it will take to dry; (2) the thinner the solution is chilled, the easier the process.

This paradox may be explained in this way: A slice of gelatine of 4 per cent. jelly weighs about 75 grams; a dried sheet will weigh 3 grams. Therefore, from one sheet of gelatine 72 grams of water must be extricated. The first 50 parts of water will be readily taken up by the air current, but after this, the surface of the gelatine sheet has already hardened to such an extent that it is more difficult for the remaining 22 parts to escape. The more concentrated a solution, the harder the surface will become during the first part of drying, and a much slower final process will be the result. On the other hand, the spreading of thin solutions requires very much more labor, a greater number of trucks and nettings, a larger space in the alleys, and, consequently, a larger investment, as will be explained in the following example based upon a production of 2400 pounds of gelatine daily. This production has been chosen, as manufacturing on a lower scale has proved uneconomical.

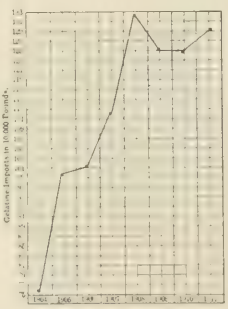
2400 Pounds (1090 Kg.) Gelatine to be Produced.	Requires 4000 lbs (1818 kg. raw material at 60 per cent.	In thin sheets at 3 gr.	In medium sheets at 9 gr.
There will be drawn off of 4 per cent. solutions.		7200 gal. (27270 liters)	
Of 12 per cent. concentrated solutions			2400 gal. (9090 liters)
On molds required	1818		606
Gelatine slices made	363600		121200
Frames and nettings required	7575		2525
Trucks required	252		84
Water to be extricated in alleys	57576 lbs.		17592 lbs.
Alleys necessary (theoretical)	10		4
Alleys necessary (practical)	14		7

After passing through the drying channels the gelatine enters into the last stage of manufacture.

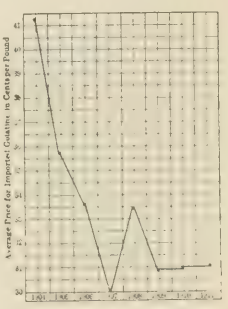
VI. The dried gelatine sheets are taken from the nettings, thrown into a crusher, running at 250 revolutions a minute, and requiring about two-horse power. The crushed gelatine, so-called "Flake," passes into a silo, from thence into a mill of the dismembrator or disaggregator type, is screened to different granulations, and barreled up in the different forms as required. For still finer powdered goods it is necessary that the gelatine pass through another mill which will reduce all the crushed or granulated gelatine to powdered form, from 50 mesh upward, according to requirements:

Proportion of power to production = HP : 12–20 lbs. gelatine (according to conditions)
Capital required for production of 1 pound gelatine = 31c. to 25c.
Consumption = 55 gr. per capita, U. S. A.

Curve I shows the imports of gelatine into the United States during the past eight years, while Curve II shows the fluctuations in price during the same period.



Curve I.



Curve II.

A PUNCH FOR STRAIGHT RUBBER TEST PIECES.

By Harry P. Mills
Received Jan. 5, 1912

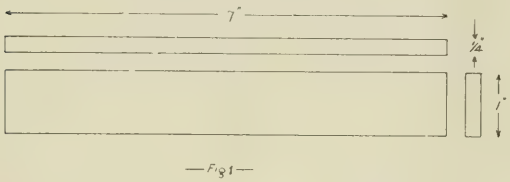
Although the ring form of test piece has recently become popular, many workers still prefer the straight test piece, as the use of the latter does not involve certain serious errors to which the ring piece is subject.

The devices for preparing ring test pieces have been perfected beyond those for handling straight pieces, and the ring pieces are therefore easier to manipulate; but by the use of the punch herein described the strip pieces can be prepared with even less trouble than the rings.

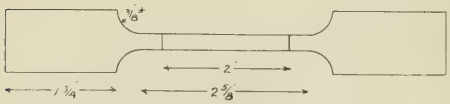
All those who have tried punching test pieces will appreciate the difficulty in preparing uniform pieces of a regular cross section that can be easily measured. The softer the stock the more it yields under the knife or punch, and the more likely will the section depart from the desired shape. Our work deals largely with pure gum stocks, and the method described has been found to work quite satisfactorily.

Several workers have attempted to mould the strips into the desired form, but it is difficult to obtain uniformity throughout the narrow portion. It is essential that the section should be uniform and easily measured; also that the edges should be clean, as a tear will readily follow a slight check. It has been found much more satisfactory to punch away the sides of a flat strip, leaving the test portion between two stout ends, as in Fig. 2.

The strip is moulded to the form shown in Fig. 1,



—Fig. 1—



—Fig. 2—

in bolted moulds, each mould producing eight strips.

The punch (Fig. 3) is equipped with a sharp, thin, curved knife, set firmly in the vertical slide. A stop prevents it from touching the cast iron bed plate. A "nest" into which the strip fits snugly prevents the rubber from spreading while being cut.

The nest is secured to the bed plate by thumb screws, and it can be adjusted to regulate the thickness of the strip.

To operate, a few thicknesses of manilla paper are laid in the nest: the knife cuts into these, but does not reach the bed plate. The strip is then placed in the nest and one side punched out by operating the pedal. The knife is so shaped that a little of the rubber at each end is left uncut; thus, when the strip is lifted out, the punched piece still adheres to it. Without removing this piece the strip is replaced in the nest, this time with the cut edge forward. Care is taken to have the same surface up in both cases, as the parallelism of the width of the test pieces is thereby assured. The second side is punched out, the strip taken out of the nest and the punched pieces

Fig. 3.
"Punch for Straight Rubber Test Pieces."

torn or cut free. Two marks at a unit distance are then placed on the strip and after measuring is ready for testing.

The strips are uniform to within a few thousandths of an inch, and the cross section is almost a rectangle, which permits of accurate measurement by platen calipers.

The knives are removable, and test pieces of various lengths and widths may be cut from strips of any thickness.

Research Laboratory,
Continental-Mexican Rubber Company,
Torreon, Coah., Mexico.

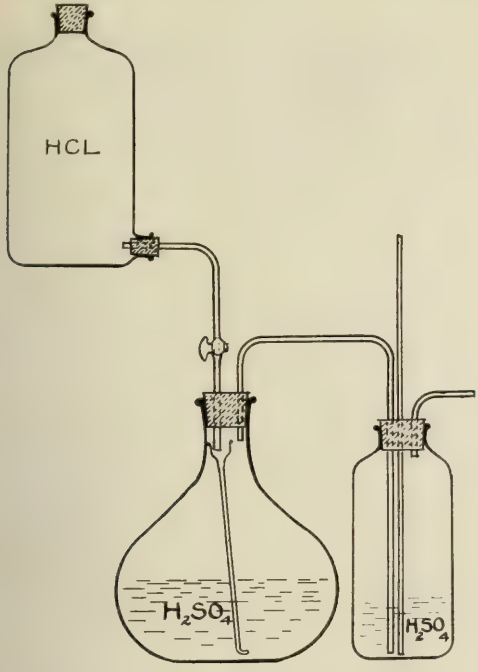
A LABORATORY GENERATOR FOR HYDROCHLORIC ACID GAS.

By Edwin Dowzard.
Received January 4, 1912.

In laboratories where dry hydrochloric acid gas is frequently or occasionally required, the apparatus illustrated in the sketch will prove of value.

On referring to sketch, the apparatus will be seen to consist of a storage bottle for commercial hydrochloric acid, a flask to be half filled with concentrated sulphuric acid, and a bottle containing concentrated

sulphuric acid for drying purposes. The storage bottle for hydrochloric acid should be not less than thirty-six inches higher than the flask.



By means of the thistle headed funnel, the lower part of which is drawn out to not more than $^1/_{16}$ inch diameter, commercial hydrochloric acid is delivered to the bottom of the flask containing concentrated sulphuric acid.

The advantages of this apparatus are that hydrochloric acid gas is evolved immediately after turning on the acid. On turning off the acid, the evolution of gas ceases within a few seconds. A steady flow of gas can be maintained for long periods of time with practically no attention.

Unless the lower portion of the thistle-headed funnel is drawn out as described above, the apparatus will not work in a satisfactory manner.

The drawn out portion should commence above the sulphuric acid in the flask.

The above apparatus has been in use for some time and has given great satisfaction.

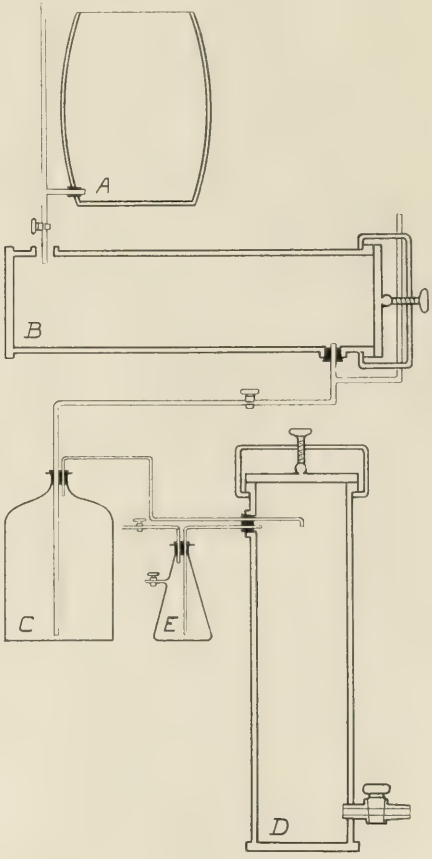
ANALYTICAL DEPARTMENT,
PARKE, DAVIS & CO.,
DETROIT, MICH.

TWO PIECES OF LABORATORY APPARATUS.

By HAROLD CANNING CHAPIN.

Received January 29, 1912.

The hydrogen sulfide generator here illustrated has been in use in this laboratory for more than two years, supplying classes of over 175 men. For an apparatus of its capacity it is simple, inexpensive, and requires but little personal attention. With the exception of the iron clamps securing the cylinder heads, and glass gauges and connections which can be put together by an amateur glass-blower, the parts are all stock articles. *A* is an ordinary ice-water tank, *B* and *D* 30-liter earthenware filter cylinders, *C* a 15-liter glass bottle, and *E* a filter flask. It is regulated by a device of Ostwald,[1] already found efficient on a smaller scale. Sulphuric acid, previously diluted in *A* with 6 parts of water, flows from *B* through glass and rubber connections by way of *C* into *D*, which contains ferrous sulphide. The gas thus generated passes through the upper outlet of *E* to the piping of the laboratory. When the supply exceeds the demand the excess gas stores itself under pressure in *C* by displacement of acid into *B*, at the same time stopping



generation until it is itself exhausted. The flask *E* catches and renders visible the overflow in case *D* fills with spent liquor. Its lower cock serves to admit air and relieve suction when liquor is drawn off through the cock on *D*. To prevent small pieces of sulfide from clogging this last outlet a layer of brick is placed in the bottom of the cylinder, and to aid distribution of the acid an inverted dish is laid on top of the sulfide. The acid reservoir *B* is placed horizontally to lessen fluctuations in the gas pressure, which is dependent upon the difference in level of the contents of *B* and *C*. The connections between

[1] *Z. anal. Chem.*, **31**, 183 (1892).

the cylinders and their covers, which are ground to fit one another, are made tight with soft paraffine.

Another apparatus, exceedingly simple but so efficient as to merit brief description, is a glass siphon for emptying carboys. It has at its delivery end a cock of the diameter of the tube, and at the bend a smaller cock through which it can be exhausted. While one arm is being sucked full of acid from the carboy the other is by the same operation exhausted, so that if the tube be of large diameter the liquid having reached the summit trickles over and fills the siphon completely.

WALKER LABORATORY,
RENSSELAER POLYTECHNIC INSTITUTE

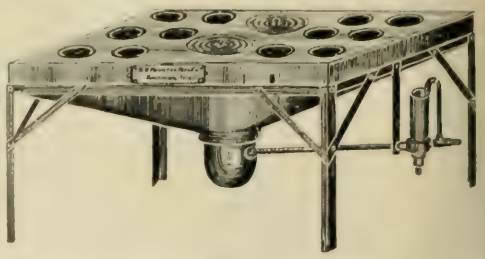
UNIQUE WATER BATH.

By S. W. WILEY.

Received February 15, 1912.

In commercial laboratories where a large amount of work is carried on and time is an important factor, the chemist has found it necessary to devise and construct time-saving apparatus. We have designed a rapid heating steam bath that combines several practical and economical features.

The bath is made of heavy copper supported on a braced stand of 1″ angle iron. The top of the bath measures 25″ by 14 1/2″, and is supported on the under side by a triangular copper stripping to prevent sagging; it contains twelve 3 1/2″ holes, and two 5 3/4″ holes, fitted with porcelain rings. The bath proper is 2″ deep at the outside edge, and the bottom makes an angle of 30° with the horizontal, reaching a depth of 4″ at the center. To the center of the bottom is riveted a threaded ring, soldered to make a tight joint. A collar fits over a cup and when connected to the threaded ring makes a water-tight joint; the cup, made of heavy spun copper with a 1 1/8″ flange at the top, measures 3 3/8″ inside diameter, and is 3 1/2″ deep. To the point of supply, 2 1/4″ above the bottom, it contains 250 cc. The cup is fed by 1/4″ brass pipe connected by means of a riveted shoulder and soldered to make a tight joint. The feed pipe is connected to a constant supply Water Level Regulator of the latest pattern.



As is often the case with municipal water supplies the pressure is freakish and the result is the burning out of expensive water baths. In this type of bath the only portion affected is the spun copper cup, which costs but a small sum and can be replaced in a few minutes.

The bath just described gives a full head of steam within three minutes, and a uniform distribution throughout the entire bath. One has been used daily for a year and a half in our laboratory, and has given the utmost satisfaction. From the standpoint of economy and upkeep, the writer feels that this type of bath may be found to be of value in other laboratories besides our own.

LABORATORY OF
WILEY & COMPANY,
BALTIMORE.

ADDRESSES

OCCUPATIONAL POISONING IN CHEMICAL TRADES.[1]

By W. GILMAN THOMPSON.

Received March 19, 1912.

In this brief discussion of the Occupational or Industrial Diseases connected with the chemical trades, either in the production, manufacture or application of chemical substances, the following subdivisions of the topic will be considered:

I. To what extent do such diseases prevail in New York City?

II. To what extent are such diseases fatal or incapacitating?

III. What measures should be undertaken to mitigate or prevent the manifold evils of the occupational disease hazards?

I. Prevalence.—Only within a very short time has any effort been made to secure accurate data bearing upon this phase of the question. In September, 1911, a law became operative requiring physicians to report to the New York State Labor Bureau all cases observed of six diseases, namely, poisoning by lead, mercury, arsenic and phosphorus, together with anthrax (or wool-sorters' disease) and the caisson disease. In January, 1912, a sub-committee for the investigation of occupational diseases was appointed by the New York State Branch of the American Association for Labor Legislation. This committee, mainly through a salaried investigator, has already gathered many interesting facts. In the past few years isolated reports have appeared in medical publications on the diseases under discussion, a number of which have been made by members of my Medical Clinic Staff in the Dispensary of the Cornell University Medical College and Bellevue Hospital, where we meet annually with many thousands of workers in all manner of trades. The latter institution, especially, affords perhaps as large an experience of this type as may be met with anywhere in this country. In the absence of extensive published data, some reference to my personal experience may be permitted, derived mainly in the two institutions mentioned and in the wards of the Presbyterian Hospital. In

[1] Read before the New York Section of the American Chemical Society, March 8, 1912, by Dr. Thompson, Professor of Medicine in the Cornell University Medical College in New York City.

the records of these three institutions, covering the past eight years, I find 283 cases of serious chronic lead poisoning, in most of which there was total incapacity for work lasting for months or years. Some of these patients had complete paralysis of the hands, many had lead colic, and most had hardening of the arteries. Some acquired chronic Bright's disease and practically all suffered from anemia, digestive disorders and muscular weakness. One youth of 23 years had been employed for eight years in a paint manufactory as a helper. He had the hardened arteries of an octogenarian, a greatly enlarged heart, diseased kidneys, and difficult breathing.

Dr. E. E. Pratt, investigating for the Committee of the Labor Legislation Association, recently found 18 cases of lead poisoning among men employed in the Brooklyn Navy Yard to scrape red paint from the hulls of the battleships.

Dr. John B. Andrews, in *Bull.* 95, of the State Bureau of Labor, reported 60 fatal cases of lead poisoning occurring in New York State in 1909–'10. Three more fatal cases recently occurred in a single smelting establishment in New York City.

Dr. Alice Hamilton, in a report on the white and red lead industry for the United States Department of Labor, found examples of lead poisoning in 33 of 56 establishments where lead was used in process of manufacture, with a yearly average of 665 cases. It is a very striking fact that in England, in the white lead works near Newcastle, compulsory medical inspection has so far reduced the cases of lead poisoning that in 1910 the ratio was 1 case among every 264 employees, whereas in Illinois, without legalized inspection and control, the ratio is one case among every 7 employees. There are fully 150 different trades in which lead constitutes a serious hazard.

With arsenic there are 27 trades in which this constituent constitutes a similar hazard. I have seen complete paralysis from arsenical neuritis, and a man employed in mixing Paris green paint came recently to my clinic with a diffuse brownish black pigmentation of the skin, derived from his occupation. The lessened use of arsenical pigments in wall papers and artificial flowers has, however, considerably reduced the number of cases of arsenic poisoning which formerly were much more common. Arsenic also irritates the hands and eyes, and produces grave digestive disorders.

Some time ago a man came to my clinic showing a perforating ulcer between the two nasal cavities, large enough to admit the forefinger, which was the result of chromic acid chronic poisoning. He had also suffered from double vision, nausea, vomiting, and difficulty in fixing the attention. On his hands were round depressed scars of old ulcers or "chrome holes" as the workmen term them. The patient, who was a chemist, had found chromic acid in the abundant nasal mucus and in his urine. There were 40 workmen employed in the chrome works with this patient, all but four of whom had chronic inflammation in the nose, and half of them had perforation of the nasal septum. A boy employed in the works had recently died in a sanitarium having violent vomiting and a yellow skin, the results of chrome poisoning. Some years ago Dr. Heise examined 176 men who had worked in a chrome manufactory in Germany; 126 of them had perforation of the nasal septum and 20 others presented ulcers which had not yet perforated. Thirty-nine men had unhealed chrome sores of the hands. Perforation has been known to occur in the nose in less than two months after entering upon the employment. "Chrome holes" may appear not only on the hands and arms, but on the feet, legs and eyelids, and sometimes on the gums and back of the mouth. Such ulcers are very slow in healing and may incapacitate the workman for many months.

Brass poisoning, giving rise to "brass founders' ague," is a well known condition among workers in moulding or founding, dipping and the filling or polishing of brass tubing and other articles of manufacture. As the cheaper grades of brass contain a small percentage of lead and tin, some of the symptoms may arise from poisoning by these metals, but the typical ague is believed to be due to the zinc rather than the copper component of brass. Doctors H. J. Schwartz and M. H. Sicard have reported in detail two cases seen in my clinic. One of the men, a brass moulder, had suffered from repeated attacks of severe chills, nausea, vomiting, sweats, headache and muscular pains—symptoms not unlike those of malaria, but unaccompanied by fever. The attacks are worse in wet or foggy weather when the fumes of the metal linger in the foundry. The other patient, a founder, had similar symptoms, and both declared that practically all their fellow-workmen suffered from time to time in the same manner. Other common symptoms among brass workers are catarrh of the stomach and bowels, nervousness and hypochondriasis. The tartar on the teeth is colored green by the copper. Brass filings, if inhaled in a dusty workroom, irritate the respiratory passages, and may give rise to "hardening of the lungs" or fibroid phthisis.

The Secretary of the Moulders' Union declares that he has found over 300 cases of founders' chills among brass workers in New York State, but as his report is not yet published, I am unable to refer to it in detail.

Mercury poisoning was formerly common among makers of mirrors, but the extensive substitution of silver in the process has lessened the number of cases of mercurialism. The latter, however, are very common among the makers of felt hats, in which manufacture mercury is volatilized in a process of hot pressing. Mrs. Linden W. Bates, in a report made for the Woman's Welfare Department of the National Civic Federation of New York, studied 102 cases of chronic mercurial poisoning. The fumes of the metal give rise to loosening of the teeth, ulcers of the mouth, diseases of the jaw bones, anemia, weakness and serious digestive disturbances.

Phosphorus poisoning acquired in the manufacture of matches has been the subject of an admirable study by Dr. John B. Andrews, of the American Association for Labor Legislation. The results of this poison,

although the cases are numerically few, as compared with those of poisoning in many trades, are more disfiguring than those of any other substance, for the phosphorus fumes entering the mouth cause decay of the teeth, and rapidly progressive ulceration and destruction of the jaw bones, which must be removed, in whole or in part, to save the victim's life. Mr. Andrews found records of 40 cases of necrosis of the jaws in a single factory "of which 15 resulted in the loss of one or both jaws and several cases resulted in death." In another small factory were records of 21 cases, 6 of which developed in a single year.

Wood alcohol, often used as a solvent in varnish, if inhaled in concentrated form, gives rise to acute poisoning, causing permanent blindness and grave disturbances of the circulation which may occasion death by paralysis of the heart. A number of fatal cases have occurred in New York City, and recently three men who went down into a large beer vat in a brewery in Buffalo, to varnish it, became overcome by the vapor of wood alcohol, with the result that two died and the third became permanently blind.

The making of pottery offers many hazards to the workmen. Those employed in mixing the damp clay suffer from bronchitis and joint pains. Those employed in applying the glaze may acquire lead poisoning, and the grinders and polishers inhale dust which may contain silica, alumina, charcoal and flint which are highly irritant to the respiratory mucous membranes, giving rise to chronic bronchitis and pneumokoniosis or fibroid phthisis. Such victims often subsequently acquire pulmonary tuberculosis, which is graphically called "potter's rot" among them.

Time does not permit a more exhaustive reference to the many other forms of hazardous chemical trades. Enough examples have been cited, however, to afford some idea of the great prevalence of the occupational disease hazards, which in many instances in this country are still regarded as necessary evils, but which, in reality, are practically all preventable by the exercise of common sense precautions, if not by enforced restrictions.

In concluding this subdivision of the topic, I will merely mention the very large group of skin diseases due to occupation, such as handling tar, creosote, paraffine, acids, alkalies, lime and many forms of dyestuffs. The resulting injuries, which are very common and may incapacitate the workman for months, include such serious conditions as ulcers, boils, a form of cancer or epithelioma, fissures and chronic eczema.

II. What is the Nature of the Disease Processes Caused by Chemical Irritants?—Apart from symptoms of acute poisoning, which are not under present discussion, the metals produce a large group of symptoms in common, besides a few special symptoms. Being inhaled in the mouth as dust or fumes, or taken into the mouth by means of food or tobacco handled by unclean hands, or in some few cases, being absorbed by the skin, they lower the tone of the blood, causing serious anemia, disorder digestion, injure the stomach and bowels and irritate the nerves, giving rise to paralysis, neuritis, and painful cramps. Moreover, constantly circulating in the blood, they produce progressive hardening of the arteries. The arteries become rigid and impose great strain upon the heart, which becomes enlarged. The kidney arteries may be affected, or the kidneys themselves irritated by the constant effort to eliminate the poison, so that in time chronic Bright's disease develops. It is these latter changes especially which constitute the most serious factor in chronic chemical poisoning, for a man with hardened arteries, an enlarged heart and Bright's disease has acquired structural changes in his system which are incurable and progressive. He may die of such lesions years after he has quitted the trade which produced them, or he may die at any time from the effects of some intercurrent disease which, under more normal conditions, he might easily resist.

With many chemicals, the insidious effects of chronic poisoning may definitely be detected at a comparatively early stage, at least before permanent disability threatens. This is notably the case with lead poisoning in which, in addition to ordinary anemia, there are specific changes in a particular variety of white blood corpuscle, a blue line of lead deposit appears in the gums, and the metal may often be detected in the urine. All these symptoms may be recognized by skilful medical inspection, even before the workman is conscious of any ailment whatever.

In another large group of cases, the hard particles of the metal dust of filings, etc., are inhaled and prove severely irritating to the respiratory passages, causing chronic catarrhs, bronchitis and cirrhosis or hardening of the lungs. These forms of irritation are not only serious in themselves but predispose to the acquisition of pneumonia and tuberculosis.

In other cases, fumes, especially of phosphorus and mercury, besides completely disordering digestion, give rise to a horribly destructive disease of the bones, as above mentioned. The various toxic gases and vapors affect chiefly the respiration and circulation, and in some instances, notably in carbon monoxide poisoning, form a destructive compound with the red blood corpuscles. Such poisons may at once paralyze the heart as in the case of wood alcohol, or cause vertigo and possibly coma as in the case of naphtha, gasolene and similar products. The various acid and ammoniacal fumes produce intense irritation and swelling of the bronchial mucous membrane, with often fatal suffocation.

III. The means of mitigation of the occupation hazards may be summarized briefly as follows:

1. A campaign of education is needed, particularly among physicians, to direct attention to the importance of recognizing the early symptoms of the chemical poisons, a matter which heretofore has been much neglected. This is already being conducted by the State Labor Bureaus, the American Association for Labor Legislation, and an increasing number of instructive articles in technical medical journals.

2. The collection of accurate statistics regarding the extent and severity of the numerous chemical industrial hazards. This work is also in progress

under the auspices of the institutions above named and the State Factory Investigation Commission.

3. The interests of chemists in devising means to render dangerous chemical trades less hazardous. Already much has been accomplished in the modern improvements in the manufacture of phosphorus matches, the elimination of lead from pottery glaze and of arsenic pigments from the coloring of wall papers, artificial flowers, etc. In France, the compulsory substitution of zinc for lead white in the manufacture of paint has accomplished great good.

4. The education of manufacturers and employers in the knowledge of the economic efficiency which immediately results from the adoption of recognized methods of proper ventilation and cleanliness in foundries, mills or factories where toxic fumes, gases, vapors or dusts are generated.

5. The education of employees in hazardous chemical trades as to the special dangers involved and simple expedients to avoid them. Such a system of instruction as that practiced by the Illinois Steel Corporation, in methods of avoidance of accidents, if applied to the avoidance of disease hazards, would soon demonstrate an equal if not greater economic value. These measures, upon which this corporation finds it an economy to expend over $1,000,000 annually, comprise furnishing workmen with printed directions, display of special danger signs, offering of rewards for compliance with regulations, the formation of committees of safety among the workmen, and many other expedients.

I see no reason why there should not be warning labels attached to the containers of paints, varnish and volatile chemical irritants of all kinds, just as we now have compulsory labeling of the contents of all containers of dangerous drugs. Such labels should state concisely the name of the hazardous chemical, the chief symptoms it produces, and the means of avoiding the hazard. For example, such a label might read: "WARNING! *This paint contains lead. If the lead reaches the mouth by means of unclean hands, food or tobacco, poisoning may result with symptoms of colic, paralysis, hardening of the arteries, or chronic kidney disease.* BE CAREFUL!" or "WARNING! *This varnish contains wood alcohol, the fumes of which, if breathed in a confined space, may cause permanent blindness, or possible fatal paralysis of the heart. Use only where there is good ventilation, and never breathe the fumes directly.*" Of course, in this case the use of wood alcohol should be prohibited altogether, but such a label might have saved the lives and eyesight of those unfortunate men in the brewers' vats in Buffalo.

6. The periodic examination by physicians of workmen using dangerous chemicals, conducted at least as often as once a month, in order to detect incipient cases of poisoning and give proper suggestions as to prevention of further hazards.

I have presented only a brief review of a very broad and most important topic, which is just beginning to attract the study and interest in this country which it has commanded abroad for many years. It is a topic which appeals alike to humanitarian, scientific and purely economic interests, for there is no one among us who does not make use of some article of necessity, adornment or luxury which has in its process of manufacture been associated with possibility of disease hazard to the workman, from the match with which we strike a light, to the glaze on our porcelain coffee cup, or the felt hat which we "throw into the ring." The problem before us is to make first a rational study of the extent and gravity of the various occupational disease hazards, and then seek to deal with them through education, invention, common-sense precaution, and, where all else fails, through appropriate legislation.

THE PROGRESS OF THE WORK ON THE REVISION OF THE UNITED STATES PHARMACOPOEIA.[1]

By J. P. REMINGTON.

The American Chemical Society, having representation in the United States Pharmacopoeial Convention, should be kept informed of the progress made from time to time in the work of revision. The subcommittee on scope have been wrestling with the problem of admissions and deletions for over one year. Their labors cannot be said to be concluded, for, although they have presented a tentative list, some modifications will be required. The convention recommended publicity under Section 14 in the Abstract of Proceedings in the following words: "It is recommended that the General Committee of Revision make public, for comment and criticism, an abstract of new descriptions and standards and of changes in descriptions and standards proposed, before final adoption."

Inasmuch as admissions and deletions would be properly included, the Committee of Revision decided to give the lists to the journals for publication. The lists have excited considerable comment and the chairman has received many communications advising the admission of this, and that, and the other, or the deletion of this, and that, and the other. The committee itself, although reasonably harmonious, are divided on the scope of the Pharmacopoeia. A small but active minority have clearly expressed the view that the Pharmacopoeia contains a large number of articles which, in their opinion, are worthless. On the other hand, a large majority of the committee are opposed to dropping so many drugs and medicines because they say they are still used in the practice in various parts of the country, and as the Pharmacopoeia is now a book of standards, they believe that the doctor and the pharmacist are entitled to have the benefit of the best quality of drugs and preparations and that this consummation will be brought about most effectually by retaining the drug or preparation in the Pharmacopoeia and attaching definitions, descriptions, and tests, so that those who do use the article may have the protection of the National and State Food and Drug Laws. It seems difficult at times for some of the members of the committee to realize that the Pharmacopoeia is intended to represent all parts of the United States and that there always will

[1] Chairman's address delivered before the Division of Pharmaceutical Chemistry, American Chemical Society, December, 1911.

be in the Pharmacopoeia many preparations which a doctor has never used and probably never will use in his life. It does not follow, however, that some other physician living in a different section of the country has not found the medicine rejected by Dr. A a most efficient remedy and Dr. B could argue with just as much force that he has no use for the pets recommended by Dr. A. This situation is a perfectly natural one and will not embarrass the committee.

So far, there has not been the slightest attempt on the part of the manufacturers of specialties protected by trade mark or copyrighted label or controlled by proprietary rights to have their goods introduced into the Pharmacopoeia. In former revisions there were slight evidences of the pride of a manufacturer to have his product paid the compliment of Pharmacopoeial recognition, but since the passage of the Food and Drug Laws it would seem that the manufacturer preferred to get along without official recognition, for this would mean that he must always maintain his product at the standard of strength and quality once established by the Pharmacopoeia.

This does not mean that he would like to lower the quality; he might want to improve it by raising the standard, or the Pharmacopoeial test for it might prove inadequate or faulty. In any event he would prefer freedom of action.

Analytical chemistry has proved to be one of the foundation stones in the building of reform structures. Without it, successful prosecution of offenders could not be maintained. The chemist has risen immensely in reputation in the eyes of the public. The labels of the manufacturer must now represent the *truth* in describing the contents of the container. False and misleading statements are no longer tolerated. This puts the honest manufacturer in the proper light. Advertising artists with imagination have prepared labels attractive to the eye in the past and they are still exploiting preposterous claims of remedies, but much more intelligence is being displayed by the public. Nowadays it is amusing to listen to the remarks of young people who ask their elders whether this or that statement in an advertising circular is really true or likely. The old idea that so many people used to have, that because a statement was in print it must be "gospel truth," is becoming obsolete. Probably no other influence has been so great in improving the quality of chemical preparations as the requirement of the Food and Drugs Act, that, if an article labeled with an official name differs in quality or strength from the standards laid down in the United States Pharmacopoeia, such difference must be distinctly printed on the label. A manufacturer in nine cases out of ten prefers to improve his product and bring it up to the official standard rather than place upon the label a qualifying statement.

The tests in the Eighth Revision of the chemical substances are undergoing careful investigation, and a number of the old tests will be deleted and new ones admitted. The sub-committee on organic and inorganic substances have their hands full at the present time in trying out the many suggestions which have come to them; it is this part of the work which will probably delay the issue of the book. Much time has been consumed in selecting the simplest and most effective methods for determining the physical factors, *i. e.*, melting points, boiling points, solubilities, specific gravities, saponification values, iodine numbers, etc. It is obvious that in a law book it is necessary to designate uniform methods for obtaining these physical factors. The figures given in the text of the book would show that they were obtained by the methods given in the book in the Introductory Notices. The question of solubilities seems to be the most difficult, as might be supposed, and the work of revising all the solubilities in the text according to the Official Method will call for much labor and time.

Every one of the sub-committee has been industrious and active, but so far, the sub-committee on nomenclature have not been called upon for their report. This is usually the last sub-committee to send in its recommendations. A number of letters have been received by the chairman urging the necessity for retaining the present system of nomenclature.

While there may be some members who desire to introduce changes, it is believed that the majority of the committee are opposed to radical changes. Of course, these members will listen attentively to all suggestions. When it is considered that millions of labels of official products are now in use and a large sum of money has been expended very lately in revising these to conform to the provisions of the law, it is believed that it would not be wise to make any change in the general form and style. But obviously any errors must be corrected, and new drugs, chemicals, or preparations introduced must have corrected titles which conform in style with those already introduced. Undoubtedly some of the names will be shortened for the sake of conciseness and convenience in printing. Abbreviations of the official titles will be introduced for the first time in the new Pharmacopoeia. These will serve as a guide to physicians and to pharmacists in labeling their stock bottles and containers.

Inasmuch as the Pharmacopoeia is now a law book, it has been proposed to print a small numeral on the left hand side of each line of the article completely down the page so that for convenience of reference one who quotes the Pharmacopoeia can indicate the page and the numbered line.

On the whole, it may be said that the work is being pushed most actively. A proper sequence and system is necessary if the valuable time of the members is not to be wasted. The immediate work of revision is entrusted to fifteen members selected by the general committee. This is called the Executive Committee of Revision and each member is chairman of a subcommittee. He and the other members of the subcommittees are chosen for their fitness to serve under their chairman. When a sub-committee is ready to make its report, the Executive Committee votes upon it and the text of the book will be framed upon the results as reported. It will be seen that, by this plan, the large number of facts accumulated in ten years

will receive minute and careful consideration by the whole Committee of Revision and probably ninety per cent. of the final work will stand as reported by these experts. If the sub-committee should make a mistake or an error in judgment, it will be pointed out by some member of the Executive Committee and a reconsideration by the sub-committee asked for. If the whole Executive Committee and the special sub-committee should differ on any question, the Executive Committee has the right under the By-Laws to appeal to the fifty-one members of the General Committee of Revision for final statement. Then again, under the plan of publicity, any one interested in the Pharmacopoeia may comment through the journals or appeal to the chairman of the Committee of Revision for a reconsideration. This plan, which differs from that used in the previous edition, is working out satisfactorily: it is constructive work on a comprehensive plan. The new Pharmacopoeia will not represent one man's work, but the best judgment of men selected by a large convention for their special fitness to perform certain duties. A Pharmacopoeia should represent as accurately as possible the *present state of knowledge* and a committee should not delay the publication of the work because some one believes he has discovered a new test or an improvement and all must wait until such has been tried out.

In the past a number of tests were introduced into the Pharmacopoeia which *had not* been sufficiently tried out by many workers. The result sometimes proved to be unsatisfactory and an old test had been discarded in favor of a new one which had practically failed. Therefore it would seem to be common sense to "hold fast that which is good." A Pharmacopoeia should represent advanced knowledge of facts known and proved at the time the book is written. There should be no guess work or hope-so's. It is far better to take no chances on an untried test, no matter how promising it may seem to be; but now that the book is the standard for the country, it is of the utmost importance that the definitions, descriptions and tests should be selected from facts which are tried and true.

The members of the American Chemical Society are requested to send at once to the office of the chairman of the Committee on Revision, 1832 Pine Street Philadelphia, any correction or suggestion which they believe will improve the present Eighth Revision of the United States Pharmacopoeia. These letters are referred first to the sub-committee having such subject in charge. They are then carefully treated under the plan outlined above and it is not likely that any comment or suggestion could be overlooked. Of course, no one can promise that every suggestion will be adopted, for many of the suggestions upon the same subject are opposed to each other. In some cases two tests for the same substance have been suggested, both of which are valuable. It then becomes the duty of the committee to choose between them, and this responsibility must be assumed by the committee. Outside assistance from experts will be freely sought. Some one who has made an especial study of an assay or the habitat of a plant, or some manufacturer, who is willing to disclose special information which he may have, will find the committee responsive and eager to accept whatever is tried and true.

Now is the time to send in all suggestions for improvement. Unfavorable criticism of the printed book will be shorn of its sting. If any one interested in the new revision holds aloof and deprives the committee of a valuable fact or hint which he has discovered, it will tend to depreciate the value of the Ninth Revision. The plan of revision is comprehensive and the system is the best that could be devised by representative convention in which no special interest has been recognized and which is not under the domination of any trust or clique.

The conclusions of the committee will be published in advance and no corporations or firms will have any privileges which would tend to give them any financial advantage over any other firm or corporation. Neither the chairman of the committee nor, as far as he knows, any other member has been approached by any one seeking such an advantage. This is undoubtedly due to the fact that advance information has gone abroad that it would be useless for any one to attempt to obtain special privileges which would be denied to others. Investigation will always prove that the confidence and the trustworthiness of the members of the Committee of Revision are well placed.

Finally, let me appeal to the members of this Society to cheerfully render every assistance in order that the new Pharmacopoeia may be the best book of its kind in the world.

CURRENT INDUSTRIAL NEWS

By W. A. Hamor.

THE INDUSTRIAL USES OF OZONE.

In a paper on the production and application of ozone, in a recent number of *Nature* (88, No. 2208, pp. 551–5), F. Mollwo Perkin states that the only method employed commercially to prepare this powerful oxidizing agent is to subject oxygen to the action of the silent electric discharge, the oxygen thereby receiving electrical energy and becoming converted into ozone. Since all the apparatus employed depends upon some method or other of obtaining such a discharge, very high electrical potential is necessary. In general, the silent discharge occurs between conducting plates separated by means of a dielectric. The original ozonizer of this type was the invention of W. von Siemens; it consisted of two concentric tubes, coated on their outside surfaces with tinfoil, the glass of the tubes acting as the dielectric. Berthelot employed glass as the dielectric and a liquid as the conducting material. Modifications of both these forms are now used commercially. The "Ozonair" apparatus consists of wire gauze as the conductor, separated by mica as the dielectric. When the ozone is to be produced for water sterilization now actually employed commercially—the

ozonizer is enclosed in an iron case; when it is to be required for the purification of the air or for ventilation, it is open, the air being drawn through the apparatus and distributed by means of a fan. The electrical tension used is about 7,000 volts. The Siemens Halske type, used for water sterilizing, consists of concentric pipes placed one within the other; the inner one is of aluminum connected with the leads carrying a high-tension current; a glass cylinder, surrounded by water circulated for cooling purposes, and "alive," is the other pole. The water surrounding the glass cylinder receives its electricity from the iron-containing box, which is earthed, and consequently forms the negative pole, while the aluminum pipe is the positive pole. The annular space between the concentric pipes is where the silent discharge occurs. The complete apparatus is composed of a cast-iron box divided into three chambers: a lower chamber for receiving and conveying the air to the ozone tubes; an hermetically sealed middle compartment into which the ozone tubes are inserted by means of a stuffing-box gland; and an upper chamber for collecting the ozonized air. An alternating current at 8,000 volts is used. The Abraham Marmier apparatus is said to employ a potential of 40,000 volts; it is made up of a number of hollow cylindrical electrodes, insulated by glass and contained in a box. The Otto ozonizer consists of a series of transverse plates, so arranged that a dielectric plate is placed between the electrodes.

The "Ozonair" process is said to be used in England for the sterilization of water. The ozonization takes place in three stages—that is, the same water comes into contact with ozone three times. The Siemens-Halske system is said to be largely employed on the continent, the largest plant erected by them being at St. Petersburg. In this plant the ozonizers are worked with a three-phase alternating current at 7,000 volts and 500 periods; and 2,000 cubic meters of water can be dealt with per hour. Other places in Europe where ozone is used for sterilizing the public water supply are Paderborn, Wiesbaden, Paris, Hermannstadt, Florence, Nice, Chartres, Villefranche, Rovigo, and Chemnitz. Two new ozone plants are said to be under installation in Paris with a daily output of 45,000 cubic meters of water. In the United States ozone is employed at Philadelphia. Perkin states that the employment of ozone for sterilizing water is "not only efficient but also very cheap. In this country (England) to sterilize 1,000 gallons of water the cost is from one halfpenny to one penny, depending upon the size of the plant and the cost of the electrical power." Ozone apparatus has also been devised for fitting on to the ordinary water mains, the ozonizer only functioning when the water tap is turned on; and by means of petrol motors, ozone may be used for sterilizing water during campaigns. Comparing the ozone process with ultraviolet sterilization, Perkin says: "For small scale work the ultraviolet sterilization is very well adapted, but ozone is better for large scale operations."

Ozonized air is said to be very largely employed in the ventilation of theatres and other large public buildings; an ozone plant is now being employed in the ventilation of the London Tube Railways "with beneficial results." Perkin recommends that the House of Commons be supplied with an ozonizing apparatus.

Ozone is now used in the manufacture of vanillin from isoeugenol; in the strengthening of weak yeast in brewing; in bleaching oils and fats; in blowing such oils as linseed oil; in bleaching delicate fabrics, and in bleaching flour. The maturing effect of ozone on wines and spirits is said to be remarkable, since spirit which requires years for aging is matured "in a remarkably short time by emulsifying with ozone." It has been suggested that ozone be used in tobacco factories to aid the maturing.

A study of the influence of ozone in ventilation has recently been published by Hill and Flack [*J. Roy. Soc. Arts*, **60**, 344 (1912)]. These authors point out that for efficient ventilation, the chemical purity of the air is of relatively little importance, what is required being air of the proper degree of coolness and humidity, and movement of the air so as to vary continually the cutaneous condition of the body. The impulsion of hot air into a room is regarded as the most objectionable of all systems of ventilation. Hill and Flack consider that the chief value of ozone in ventilation lies in its effect on the olfactory nerves and those of the skin and respiratory tract. The concentration of ozone must be very low (less than 1 part per million).

Perkin failed to note that there is an ozone plant at Great Falls, S. C., which handles 80,000 gallons of water per 24 hours (*Eng. Record*, **64**, 12); that there are various methods of applying ozone to ventilation, cleaning and sterilizing purposes in the brewery (Vetter and Moufang, *Wochschr. Brau.*, **28**, 377); and that ozone has been tried as a sterilizing agent for milk, cream, butter and soft cheese, with hardly desirable results (Freund, *Chem. Ztg.*, **35**, 905). Another discussion on the applications of ozone is contained in *L'Industria Chimica*, 11, 121–3. On the preservation of food and medicine by means of ozone, see Linder, *Chemical Engineer*, **12**, 61.

NON-FREEZING MIXTURES.

The prevention of freezing in water pails and chemical fire extinguishers is discussed by Robinson in a recent paper (*Ind. Eng.*, **11**, No. 4, 310), and some important data are given.

Fahrenheit Freezing Points of Solutions Containing:

Lbs. per gal.	Sodium chloride.	Calcium chloride.	Lbs. per gal.	Sodium chloride.	Calcium chloride.
0.5	24°	29°	3.5	— 8°	— 8°
1.0	18	27	4.0	.	—17
1.5	12	23	4.5	.	—27
2.0	6	18	5.0	.	—39
2.5	1	4	5.5	.	—50
3.0	—3	—1	...	.	..

Calcium chloride is superior to sodium chloride in that it does not corrode steel tanks and barrel hoops. When calcium chloride is used, wooden barrels should first be well coated inside with asphaltum or a mixture of paraffin and resin, to prevent shrinkage of the staves. Calcium chloride attacks solder, and is therefore unsuitable for use in extinguishers of metal. A 40 per cent. solution (specific gravity 1.4) can be purchased on the market; when this is diluted with an equal quantity of water, the solution will not freeze at —9° F. It is recommended that when automatic sprinkler systems are installed in warehouses or other places of exposure during winter, a calcium chloride solution be used, as this will do away with the necessity of maintaining a dry-pipe system and its attending risks, due to leaky valves and possible failure of the air supply. The system should be filled with a solution of 1.225 to 1.25 specific gravity (3.36 to 3.76 lbs. of calcium chloride per gallon of solution), and a check valve installed to separate this from the source of the water supply.

Glycerine has been recommended for use in extinguishers, the addition of $3\frac{1}{2}$ qt. to a standard extinguisher making a solution capable of withstanding —4° F., and 4 qt. a temperature of —10° F. It tends to disintegrate rubber, however.

Denatured alcohol—water solutions are stated to have the following values: 20%, 10° F.; 30%, —5° F.; 40%, —20° F.; 50%, —35° F.

A NEW LIQUID MIXER.

The liability to use an excessive quantity or an insufficient amount of solutions of chemical reagents for the purposes of precipitation, neutralization, or purification in manufacturing processes where the financial side of the matter is an important factor, renders the question of economy in weighing or measuring such reagents a point to be accorded careful consideration. It is reported (*Chem. Trade J.*, **50**, No. 1299, 411) that an ap-

paratus, which is self-acting and requires very little attention in its use, is being placed on the market by a London firm for the chemical treatment of water and trade effluents, in which the exact proportions of reagents are maintained, it is claimed, notwithstanding any change which may occur in the rate of flow of the liquid under treatment. The apparatus is said to be adapted to deal with large quantities of liquid, and if constructed on a small scale may prove useful in other ways. The crude liquid to be treated passes under slight pressure through a pipe leading to the purifying tank. A portion of the pipe being constricted at one point like the Venturi tube allows the liquid to flow at this point at a greater velocity than in the full-sized portion; consequently, as the velocity increases, there is a corresponding decrease of pressure in the narrower portion, which is connected with two vertical pipes, each containing a float of a material heavier than water. A cylindrical vessel containing the reagent is attached to these floats by a lever, and the change of pressure is used as the power for setting the apparatus in action. When the apparatus is at work, the liquid in the two vertical pipes stand at levels depending upon the velocities of flow in the two portions of the Venturi tube, the difference of these two levels determining the amount of reagent entering the main stream. It is claimed by the manufacturers that under the most extreme conditions, the error in use will not exceed 1.7 per cent.

THE STERILIZATION OF POTABLE WATERS.

In a paper on the "Sterilization of Drinking Waters by the Action of Ozonized Oxygen and of Chlorine Compounds in the Nascent State," presented before the Paris Academy of Sciences (*Compt. rend.*, **154**, 447), Rouquette states that sodium hypochlorite was successfully employed for the sterilization of water during a recent cholera epidemic. Water containing 15,000 *B. coli* per liter was rendered sterile by the addition of 1 mg. of active chlorine per liter containing 1 mg. of organic matter. Rouquette states that the best form in which to use active chlorine for this purpose is as a mixture of one part of the salt $Na_2S_2O_9$ (obtained by mixing hydrogen dioxide and sodium hydrogen sulphate in concentrated solution) and two parts of the compound Na_2O_2Cl (prepared by the addition of sodium sulphate to calcium hypochlorite solution, the calcium sulphate being removed by filtration). The mixture is added in the proportion of 0.02–0.1 part per 100,000, according to the degree of bacterial contamination. It is said to be more rapid and intense in action than sodium hypochlorite, and the water thus treated is reported to be odorless and tasteless, and to contain no chlorine, hydrochloric acid or sulphuric acid.

PORTLAND CEMENT.

A review of the contributions of E. Leduc to the constitution and formation of Portland cement is contained in a recent number of (*Nature*, **89**, No. 2216, 177), and many useful data, with few speculations, are given.

Concerning commercial cements, the fact recognized in practice, that the mechanical strength falls off rapidly as the content of clay is increased, is confirmed in Leduc's "Sur la Constitution et la Formation du ciment Portland," and it is also shown that the coarseness of grain of both clayey matter and of sand has at least as great an influence on the "falling" of clinker as has the amount of their constituents. A normal clinkering temperature is set down at 1400–1450° C. Leduc shows that cements in which the alumina is replaced by ferric oxide are mechanically weak, and found that those containing large amounts of magnesia (*e. g.*, 25 per cent.) went to pieces on exposure to steam. "It should be noted that Leduc took unusual pains to bring his raw materials to an extremely fine state of division, fully comprehending that in a mass which is almost plastic the occurrence and completion of the reactions concerned in the production of definite silicates, aluminates, and the like are dependent on the intimacy of admixture, as well as on the temperature and the time. Any one who has prepared Portland cement experimentally knows that particles of sand which may be only 0.1 mm. in diameter will each produce its small center of 'falling,' the dicalcium silicate oozing forth from the site of the grain...., whereas the same raw materials, really finely ground, will not 'fall' at all."

In collaboration with Chenu, Leduc has shown that Seger cones, useful as they are for a number of purposes, are far from exact as temperature indicators; that they may well be used side by side with materials of the same class which are to be heated in the same way, but that in all cases they must be checked by whatever kind of pyrometer is best adapted for the temperatures to be measured.

BLEACHING POWDER AS A SOAP SUBSTITUTE.

According to *Scientific American Supplement* (No. 1897, 304), a German physician, Sacher, recommends the use of bleaching powder as a cleansing agent for the hands of workmen as a preventive agent against metal poisoning. Working men handling metals, such as lead, mercury, antimony, arsenic, bismuth, zinc, chromium, or manganese, either in metallic form or in the form of compounds, are constantly exposed to the danger of poisoning, through imperfectly cleaned hands. Small particles may thus be transmitted to the mouth in eating or using tobacco. To completely remove metallic impurities from the hands is sometimes difficult; soap alone is generally useless, especially since it forms insoluble compounds with most of the metals. Bleaching powder, however, is said by Sacher to be an ideal material for the purpose; it has no injurious effects, when properly used, and acts chemically as well as mechanically. It forms a saponaceous lather and has the further advantage of possessing strong disinfecting properties.

WATER-GAUGE GLASSES.

All users of steam boilers are familiar with the trouble which is occasionally experienced in connection with the glasses used in water-gauges as the result of the corrosion or wasting of the ends of the glass tubes inside the glands of the fittings. Efforts have been made to get over the difficulty, and many different kinds of glass have been tried, but only a partial measure of success appears to have attended the experimentation, while the rapidity with which the glass is attacked has increased as steam pressures have become higher. The corrosion is always worse at the steam end of the tube than at the water end, and has often led to accidents. According to *Engineering* (**93**, 499), in order to prevent this destruction of the glass, a Berlin concern has recently brought out a method for protecting the ends of the tubes. This is said to be accomplished by providing the tube, on the inside and outside of its ends, with a metal protective coating which yields to the expansion of the glass. This is united to the glass by means of a cement that forms a compact whole, which, it is claimed, can not be dissolved by water. For normal pressures, the glasses are provided with a metal sheath at the steam end; while for high pressures and for water high in alkalies, the tubes are provided with metal coatings at both ends.

PACKING IN STEAM PLANTS.

Packing for cylinder heads, steam chests, pipe-flange joints, valve stems, etc., is now regarded as indispensable, and the engineer has quite a large line of packings to select from. According to *Power* (**35**, 545), the development of the manufacture of packing has proceeded hand-in-hand with the utilization of steam. Up to 1850, for example, the commonly used material was a composition containing red lead, hemp and oil, made into a putty. About 1860, cloth insertion packing was introduced;

it consisted of rubber composition with insertions of duck or sheeting, and was used between 1860 and 1875, when the steam pressure did not exceed 80 pounds per square inch. Afterwards came plumbago and rubber compositions, termed "self-vulcanizing" packings; these were found to be more durable and satisfactory under the conditions then existing than the preceding, but had the disadvantage that they had to be baked into the joint. In 1886, several semi-vulcanized rubber-composition packings appeared on the market, and a composition of rubber and asphaltum, suitable for liquid conditions, was next introduced. During the period 1900 to 1910, steam pressures have increased from 80 to 200 pounds and over in stationary plants. This increase brought a corresponding rise in temperature, which was further increased by the practice of superheating. Then, too, the wider use of the air compressor, ice machines, gas engine, superheater, etc., created extreme temperatures demanding a packing which could meet exacting conditions. It is said that composition packings have been perfected which possess great resistance to extreme heat as generated under high pressure. The basis of the material is pure asbestos fiber, the fibers being treated with a waterproof compound to prevent the absorption of water. The treated fibers are compressed into sheets, pliable, resilient, and of high tensile strength.

DEVELOPMENTS IN STEAM GENERATION.

In the United States the employment of measuring instruments in the boiler room has rendered it possible to make the boiler conform more closely to the load curve than formerly. H. G. Stott points out in the *Electric Railway Journal*, **38**, 781, that the Venturi meter for measuring the feed to the individual boiler; the Pitot tube in the steam pipe for giving a general indication of the relative amount of work done in different boilers; and a coal-measuring instrument in the chute or downtake coal pipe, have been used along with forced combustion. He studied the records of one-minute indications of steam and water-flow meters to show the variations in power due to variations in load. To meet these variations, it is recommended that the boiler room should be designed for maximum operating conditions and economy at average load, and to sacrifice slight economy at light loads by working only one of a pair of grates to each boiler, the other being banked; or to employ the auxiliary use of liquid fuel; or to have grates capable of working with natural draught up to a given power and thereafter with forced draught.

THE CONTACT PROCESS OF SULPHURIC ACID MANUFACTURE.

Wieland [*Ber.*, **45**, 685 (1912)] has studied the catalytic conversion of sulphur dioxide into sulphuric acid. When palladium black is exposed to moist sulphur dioxide, air being excluded, and the excess of sulphur dioxide is afterwards removed by carbon dioxide, sulphuric acid is found in the palladium, which can only have resulted by the removal of hydrogen from sulphurous acid:

$$H_2SO_3 = H_2 + SO_3; \quad SO_3 + H_2O = H_2SO_4$$

The equivalent hydrogen was not found, but, instead of it, sulphur; and Wieland has found that palladium-hydrogen does reduce aqueous sulphurous acid:

$$SO_2 + 2H_2 = 2H_2O + S$$

He therefore suggests that the ordinary contact-process of sulphuric acid manufacture is not a direct oxidation, but a reaction similar to the above, in which the function of the oxygen is to oxidize the hydrogen produced, forming the water which is itself necessary for the reaction to occur:

$$SO_2 + H_2O = H_2SO_3 + SO_3 = H_2; 2H_2 + O_2 = 2H_2O$$

FORTOLINE.

In 1910, K. Hadorff (French Patent 416,325, April 27, 1910) devised a fuel "for increasing the power of internal-combustion engines," consisting of "benzene picrate" (prepared by dissolving picric acid in benzene, heating for a prolonged period, and finally separating the excess of benzene by distillation) mixed with benzene or other liquid hydrocarbon. This fuel was said to burn without the formation of any deposit in the cylinder.

The fuel claimed in First Addition, dated September 25, 1911, to French Patent 416,325, termed "Fortoline," contains nitrobenzene in addition to "benzene picrate." 10 parts of benzene are mixed with 0.5 part of nitrobenzene to which a small quantity of picric acid has been added, and the resulting mixture is boiled for a long time. The product is added to 10 times its amount of petroleum, naphtha, petrol, benzene, or other hydrocarbon, and is claimed to "increase the power of internal-combustion engines" when the treated fuel is used therein.

THE UTILIZATION OF STORAGE BATTERY SLUDGE.

The sludge of lead peroxide and sulphate which accumulates during long periods in lead batteries has a value on account of its lead content, but its transportation to lead smelteries has been expensive and difficult because of the associated acid. Moreover, washing and pressing are out of the question because of the fine state of division of the lead peroxide. In German Patent 236,343, it is claimed that these difficulties are overcome by mixing the sludge with slaked lime; the mixture quickly sets to a firm cake. An alternative plan is to mix the sludge with the sulphite liquor from sulphite cellulose works, the lead peroxide being thus converted into lead sulphate; molasses may also be employed for the reduction of the peroxide. So much heat is liberated during these reactions that considerable of the water is evaporated.

THE MANUFACTURE OF WHITE LEAD.

It is reported (*Chem. Trade J.*, **50**, 386) that the West German Lead Color Works are now in the possession of a new process for manufacturing white lead which does away with the difficulties of dissolving the lead, encountered in the old Dutch process. Finely divided lead (readily obtainable now in a uniform state) is put into a chamber, acetic acid is added, and air is led through for agitation: a large amount of lead becomes soluble. The lead solution is then subjected to the action of carbon dioxide under pressure in another chamber, and the lead lye and white lead formed are removed by atmospheric pressure. The method can be worked in a few hours instead of weeks, and, furthermore, no lead residues are left and less acid is used.

In German Patent 244,509, recently issued, a novel process of making white lead is claimed. Litharge is treated with a boiling solution of amino acids, such as result upon the hydrolysis of albuminoid substances, and the lead is precipitated by a current of carbon dioxide. Since the organic acids remain in solution, the liquor can be used continuously for dissolving more litharge.

THE PURITY OF COMMERCIAL METALS.

Mylius (*Z. anorg. Chem.*, **74**, 407) suggests that instead of the existing irregular nomenclature ("pure," "puriss.," etc.) for denoting the purity of commercial metals, a system of numerical classification be employed. According to this plan, the first degree of purity would represent a metal in which the total true impurity, with the exception of oxygen and the products of atmospheric corrosion, was from 1–10 per cent.; the second

degree from 0.1–1 per cent., and so on to the sixth degree. It is stated that as technical products of the fourth degree and upwards (less than 0.01 per cent. impurity), the following metals may be obtained: cadmium, copper, gold, lead, mercury, platinum, silver and zinc. Zinc, cadmium and tin (Kahlbaum) have all risen from the third to the fourth degree since 1895. Redistilled zinc was found to contain from 0.007–0.0088 per cent. total impurity, whereas a sample of electrolytic zinc costing ten times as much contained 1.3 per cent. of zinc sulphate, about 6 per cent. of zinc hydroxide, 0.02 per cent. of insoluble silicate, and 0.04 per cent. of metallic impurity.

THE COST OF CHLORINE.

The following costs per ton of active chloride are compiled from a recent paper by Kershaw (*Chem. Trade J.*, **50**, 330, 385):

Method of preparation.	Form of combination.	Cost.	Remarks.
Chemical.	Calcium hypochlorite.	$68.82	Taking 3 tons 35% bleach and assuming 5% loss of chlorine.
Chemical.	Sodium hypochlorite.	98.62	Using sodium sulphate to decompose calcium hypochlorite.
Chemical.	Sodium hypochlorite.	$109.96	Using sodium carbonate, *ibid.*
Electrolytic.[1]	Sodium hypochlorite.	$106.33	6.07 kw. hrs. and 6.0 kg. salt per kg. chlorine; 15 kg. Cl per 10-hour day.
Electrolytic.	Sodium hypochlorite.	$112.13	Power at $0.008 per kw. hr.
Electrolytic ("Hermite" electrolyzer).	Sodium and magnesium hypochlorite.	$392.28	Actual cost at Poplar, England, where 50,726 gal. of hypochlorite solution were produced (1910).

SYNTHETIC ORGANIC DYES AND PATENTS FOR THE MANUFACTURE OF THE SAME, 1907-'11.

(Lehmann, *Chem. Ind.*, **35**, No. 7, 207.)

	1907.		1908.		1909.		1910.		1911.	
Groups.	Dyes.	Patents.	Dyes.	Patents.	Dyes.	Patents.	Dyes.	Patents.	Dyes.	Patents.
Nitro	..	..	..	..	..	1	..	1	..	..
Azo, substantive	54	5	123	14	85	23	92	13	72	19
Azo, acid	35	11	38	11	37	6	58	27	50	18
Azo, chrome	37	20	52	8	38	10	44	19	37	7
Azo, basic	1	2	..	..	..	..	..	1	..	1
Azo, varnish	5	6	19	9	11	11	13	15	8	7
Azo, "ingrain"	2	11	3	4	2	5	3	7	1	7
Triphenylmethane	8	5	7	5	3	9	11	10	9	14
Pyronine	4	..	2	2	4	1	..	..	3	1
Acridine	1	..	..	..	..	..	..	..	1	1
Nitroso	1	..	..	..	2	2	..	..	1	1
Anthracene	16	32	13	40	30	54	13	50	24	93
Indophenols	..	3	..	..	..	..	..	..	..	3
Oxazine	..	6	6	13	4	8	2	6	4	5
Thiazine	..	2	..	..	..	.	1	..	..	..
Azine	..	7	2	1	..	4	1	..	5	3
Quinoline	..	..	2	1	..	..	1	..	.	.
Indigo, Thioindigo	4	28	15	59	15	45	21	47	8	90
Sulphur	37	16	64	24	40	12	45	21	22	7
Constitution, unknown	2	3	1	1	..	2	..	2	..	3

THE MANUFACTURE OF ALUMINUM FOIL.

Aluminum foil is now being manufactured at La Praz and Charleville-sur-Andelle by a French company, and at Ludwigshafen a. Rh. by a German concern. The German product, termed "Alolit-foil," is being marketed as a substitute for tinfoil, and is said to be "from pure aluminum, and to be lead-free and non-poisonous."

Guillet [*Rev. Met.*, **9**, 147 (1912)] has given an account of the processes conducted in France for the manufacture of aluminum foil. The metal, delivered to the works in the form of ingots, 700 × 320 × 120 mm. (cast at 750°–775° C.), is first hot-rolled at 420° C. to a thickness of 3.5 mm. and then cut into strips 8 cm. wide, which, after being annealed at 420° C., are cold-rolled to 0.04 mm. in six stages, further reduction in thickness being then effected by continued rolling or by hammering. In the former case the metal bands are first greased, then rolled in pairs to 0.02 mm. and subsequently in fours to the desired thickness of 0.01 mm., the foil thus being had in lengths of about 16 m. In the latter case the bands are made into packets of 500 each and beaten by pneumatic hammers, each packet being placed between two thin sheets of zinc; when the thickness of the metal reaches 0.03 mm., the packets are hammered in pairs to 0.02 mm., and finally in fours to 0.01 mm. The waste in either case is considerable, only about 33–35 per cent. of the 0.04 mm. metal employed being obtained as good foil 1 sq. m. of which weighs about 27 grams. The waste foil is employed for the production of aluminum powder. Prior to trimming and cutting to size, the sheets of foil are mechanically separated. In the manufacture of aluminum powder, the comminution of the waste foil is conducted in stamp mills in which the closed mortar-box is provided with a circle of 12 stamps actuated from a central shaft.

SOME NEW "NON-CORROSIVE" ALLOYS.

The American market now affords a grade of sheet steel known as "Vismera," possessing the following composition: Iron, 99.542 per cent.; copper, 0.200; manganese, 0.190; carbon, 0.036; phosphorus, 0.004; sulphur, 0.018; oxygen, 0.009; and hydrogen, 0.001. Particular attention is called to the copper and manganese content, and to the low percentage of oxygen. It has been known for some time that the presence of a small amount of copper increases the resistance of steel to corrosion, and that cupreous steel is more resistant to acid mine waters than ordinary steel. It is said that another producer has succeeded in obtaining "an alloy steel that will successfully withstand tests with sulphuric acid, the chief enemy of tubing and sheets."

Gaston Jacquier, of Belgravia, Transvaal, has patented an anti-corrosive alloy said to be suitable for employment in the manufacture of tanks, piping, ropes, valves, pumps, etc. (U. S. Patent 1,019,963, 1912). It is made of the following metals: Aluminum, 92 per cent.; bismuth, 2 per cent.; copper, 5 per cent.; and silicon, 1 per cent. The composition may also be as follows: Aluminum, 91 per cent.; bismuth, 2 per cent.; copper, 5 per cent.; and magnesium, 2 per cent.

KUPRONIZING.

According to *Engineering* (**93**, No. 2411, 367), a London firm mainly concerned with copper-plating wood applies the name "kupronizing" to the process it employs. In the plating of wooden hand-rails, the wooden core is first impregnated with a preservative material and then flashed with either plumbago or a metallic salt. The actual copper deposition is then carried out in a bath in the usual manner. It is the present practice to deposit a layer about $^1/_{16}$ of an inch thick. Iron window-frames and iron pump-rams are now kupronized, and the process gives a copper layer which adheres so that the pieces may be machined after the copper is in place.

[1] To produce one ton of active chlorine per day, with the cheapest of the electrolytic cells described by Kershaw, would require 50 electrolyzers and involve a capital outlay of about $37,500, while the more efficient and expensive types, wherein platinum-iridium electrodes are used, would cost double this amount.

NOTES AND CORRESPONDENCE

THE GERMAN PATENT SYSTEM.

The laws regulating the protection of intellectual property in the German Empire are of relatively recent date. Previous to 1870, some of the many Kingdoms and petty states, forming now the modern German Empire, had special laws to that effect. However, all these laws proved to be rather ineffective in view of the relatively small extent of each individual state. Only the peace of Frankfurt, which established the national unity of Germany, removed this condition of affairs, which had for so many years handicapped technical and scientific progress in Germany. The new constitution expressly provides that the protection of industrial property is under the jurisdiction of the Empire. Since then, a series of broader laws has come into force, among which the patent-law is undoubtedly the most important one. This law has had a predominant influence upon the unprecedented rapid development and high standard of German industries. The number of native and foreign inventors applying for patents, increases from year to year; it is a noteworthy fact that among foreign applicants, *American inventors predominate*. It may, therefore, not be without interest, for Americans, to know the broad outlines of the principles and rules of practice and procedure of the German Patent Law.

In Germany, a patent is regarded to be equivalent to a promotion of national knowledge by the disclosure of a heretofore unknown art. The inventor is judged to be a kind of teacher to the nation. Therefore, the Patent Office does in no way care for the real father of an invention. To the first applicant is allowed the patent, and lack of first and true inventorship does not invalidate or bar the grant of a patent unless the invention has been fraudulently obtained, or stolen. If in this case, the person from whom it was stolen files an opposition at the proper time, or starts an annulling suit against the granted patent, the patent is refused or annulled. Moreover, under certain conditions, a fraudulent patentee may be compelled, by a lawsuit, to assign the patent, or even the patent application to the original owner.

This broad principle regulates easily the status of persons who have actually carried out the invention previous to a patent application by another, as well as the question of interfering applications: Such persons are not affected by the patent, for they have not been instructed by the inventor; in other words, they have not derived any new or useful knowledge by the disclosure of the patent. Therefore, they have a legal right to use the patent for their own business, but this right can only be assigned to others, together with the transfer of their whole business. In other terms, they are entitled to a limited free license. Patents filed later on for the same subject matter, for which a former application was filed, are simply refused, if the earlier application results in a patent. So all the interfering applications are rejected in favor of the first applicant, even if they are based on inventions that have been conceived at an earlier date. This, of course, stimulates inventors to apply for a patent without delay, and gives the public the benefit of early disclosure; it excludes expensive and complicated interference proceedings, and prevents applications from being kept pending in the office, for endless years, as frequently happens in the United States. It, furthermore, prevents anybody engaged in a business which is based or not on patents, being threatened at any time with unexpected destruction of business, on account of some hidden or creeping patent applications which, several years later, develop into interference proceedings.

Every application for a patent is examined by an examiner just as in the United States, and substantially along the same lines; on the average, the requirements as to inventive quality are more rigid. If an application is in the proper shape, and patentable according to the examiner's opinion, he forwards it to a Board of Examiners for a preliminary decision. If the Board of Examiners, which is composed of at least three examiners, judges that the invention is not patentable, they reject the application, in about the same way as in the United States. Otherwise, they issue the so-called decision of publication; that is to say, they apply for a supplementary public examination by publishing the title, filing date, name and residence of the applicant in the "Reichsanzeiger," or official journal. Numerous technical periodicals reprint this publication for their readers, and thereby inform the public that the Patent Office is about to grant a patent on the published invention.

At the same time, the drawings, models, specification, and claims are rendered available to public inspection for a period of two months. During that time, anybody can file a written opposition against the grant of a patent. In this way, the inventor, as well as the public, is guarded against the issue of invalid patents. Anybody, in any part of the world can file such an opposition without any costs. The law prescribes only that the opposition be filed in German language and before two months and that it embody the necessary argument. In this way, no individual who can show that the grant of the patent is unjustified is withheld from formulating his arguments, unhampered by any other formality than the mere writing and stating of the argument,—all this without the necessity of passing through the intermediary of an attorney. Opponents who file their opposition too late are not considered in the further proceedings, though their information may be given consideration by the examiners in their final decision.

If no opposition has been filed within a two months' period, the Board of Examiners issues a second decision by which the patent is finally granted; thereupon the specification is printed and published, just as in the United States.

If an opposition has been filed in due time, the opponent thereby becomes a party of the further legal proceedings. He gets information of all the arguments of the applicant and, *vice versa*, the applicant is kept informed of all opposition arguments and the names of his opponents; after the situation has been cleared up, the Board of Examiners decides whether or not the opposition was justified and whether the patent shall be allowed as presented, or allowed with restricted claims, or refused entirely.

During the whole period of examination, up to the final grant of the patent, the Patent Office can, if it deems it necessary, hear witnesses. However, all testimony is taken by the office itself, or, if the witnesses live at distant points, by the courts of justice in that district, at the request of the Patent Office, which prearranges and formulates all the questions to be put before the witnesses. No opponent or applicant can be a witness in his own behalf, nor has he any influence upon the decision of the office, and the latter alone decides what witnesses shall be heard and which not. All these questions are decided by the Board of Examiners as far as the interests of the applicant and the public may require, and no appeal is admitted against such a decision. Furthermore, no costs can be charged by the Patent Office for taking testimony, even if such testimony has to be taken in German colonies or in foreign lands, under the provision of the Convention of The Hague. Taking testimony by lawyers as in the United States, in the presence of a notary public, is unknown in Germany, and depositions of witnesses that are obtained in this way would be without any consideration whatever before the German courts.

This same way of taking testimony is followed in all pro-

ceedings whether they be for annulment, for compulsory license, or for revocation, as I shall describe hereafter.

If the grant or rejection of a patent has been agreed upon by the Board of Examiners, every applicant or opponent who feels himself injured by that decision can still file an appeal to the Board of Appeals, composed of five officials. The Chairman of this Board of Appeals is the Commissioner of Patents, or the so-called "Praesident," or in his absence, one of his legal representatives. The Board of Appeals reëxamines the whole case and its decision is final.

The life of a patent in Germany is 15 years, which begins with the day succeeding the filing day. The protection it confers becomes effective on the day of publication of the invention in the Reichsanzeiger; from that day on, the inventor can sue infringers, or the public can start a suit for a compulsory license against the inventor. It is obvious that the effective life of a German patent is therefore always shorter than 15 years, and can be badly shortened by any retardation in the issue of the final decision of allowance. In average, if no opposition is filed, and no other complications are met, about two years are absorbed, until the patent is finally granted. This represents one of the most serious defects of the German patent system, but very probably the next revision of the patent law which can be expected in 1914 will remove this deficiency.

The maintenance of patent rights depends, furthermore, upon the payment of certain yearly taxes, small during the first years, but increasing from year to year, and upon the non-payment of which the patent lapses without possibility of reinstatement. A patent lapses at once if the patentee renounces to it by written declaration.

Other persons can remove a patent right only by a suit for annulment or for revocation; such suits are brought before the Annulment Board of the Patent Office. This provision represents one of the predominant differences over the American system, inasmuch as no court is entitled to discuss the validity of a patent, as long as the patent has not been annulled by the same Patent Office by which it was granted; the courts have to take the patent as it stands and it is only left to them to interpret it in a broad or narrow sense, if the scope of the claims is unclear.

Fraudulent possession of an invention is always a reason for annulling a patent, if the annulment suit is started by the injured party; suits for annulment on account of lack of invention can only be instituted within the period of five years after publication of the final grant of a patent in the "Reichsanzeiger." After expiration of this term, the patent stands valid and unassailable. Probably this latter provision will be canceled before long, in as far as it has caused many inconveniences and injustices to the public.

Appeals against the decisions of the Annulment Board are not decided by the Board of Appeal, but by the highest court in Germany, the Reichsgericht in Leipzig. In all the legal decisions in patent matters, the "Praesident" of the Patent Office has no other intervention than to act as the Chairman of the Board of Appeals and of the Annulment Board. He is never Chairman of the Board of Examiners, and his other official functions are more of an administrative character, at least as far as patent matters are concerned.

Apart from annulment suits, the Annulment Board and the Reichsgericht decide all the actions for the grant, of a compulsory license, or the revocation of patents. Up to May 1, 1911, a patent could be revoked if it were not worked in Germany, or if, in spite of the offer of reasonable royalties and deposit of a guarantee, the patentee refused the grant of a license, provided such a grant were advisable for the public interest. Influenced by the introduction of the new revocation practice in England, and since a decision of the Reichsgericht in a revocation suit against an American patentee, it was held by the court that by reason of the German-American treaty of February 23, 1909, no American could be compelled to work his patents at all in Germany; it even was decided, if the patent was assigned to an American after the revocation suit had been started, these compulsory working provisions did not apply to him.

Under later provisions, Germany has no longer compulsory working of patents, to whatever nationality the patentee may belong. But any patentee can be compelled by decision of the Annulment Board to grant a license in exchange of payment of reasonable royalties, and deposit of a guarantee, provided such a compulsory license is conducive to the public welfare, all this regardless of the actual working or non-working of the patent by the patentee or other persons. However, it has not yet been decided, and it is doubtful whether, in view of the above-mentioned American treaty, patents which are owned by Americans are met by the new provisions of the law. Revocation of patents on account of non-working is now possible only if the patent is worked exclusively outside of Germany, but even then this does not seem to affect American patentees on account of the existing treaty.

As the courts are not allowed to discuss the validity of patents, a suit against infringers is relatively simple. Unintentional or careless infringers can be sued for damage, but intentional infringers are moreover liable to fine and imprisonment on motion of the patentee or his representatives to the public prosecutor (Staatsanwalt). Preliminary and final injunctions can be issued, or an infringer can be sued first so as to compel him to acknowledge that he actually infringes a patent. On the other hand, a similar acknowledgment suit can, under certain conditions, be started against the patentee, so as to compel the latter to acknowledge non-existence of infringement by another party. The defeated party has to pay the expenses and costs of the winning party. All these infringement suits are decided in open court before civil courts. Upon appeal, they are finally decided by the Reichsgericht, so that practically all the questions of predominant importance are decided by one and the same court. Infringement suits are relatively rare, and by no means so frequent as in the United States. Furthermore, they are considerably less expensive. The time consumed for reaching a final decision in an infringement suit depends, of course, largely upon the complications of the subject matter, the necessity of making experiments, etc. Most of the courts in industrial districts in Germany have special departments to which are assigned all cases concerning the protection of patents and of intellectual property in general.

HERBERT F. WERTHEIMER.

ORIGINALITY OF INVENTIONS.

Patent Law Reform is at present the subject of discussion in several foreign countries as well as in the U. S. The German Scientific Societies' Journals are full of criticisms and suggestions for improving the present status of the patent law. It should be interesting to Americans to watch the situation abroad as the American and the German Patent Laws are the best national laws to guarantee the rights of the inventor and to stimulate the progress of industry. The highly developed state of industry in both of these countries is the best proof that their Patent Laws rest on a sound basis.

Comments on the U. S. Patent Law by our leading inventors have shown that it is largely in matters of appeals, interferences, infringements and the like proceedings where reform is urgently needed. One extremely important complaint about the U. S. Patent Office has been overshadowed by the discussions and suggestions in regard to a U. S. Patent Court of Appeals.

American inventors who have had experience with German patents are usually much pleased with the strict impartiality and business-like methods of the German Patent Office in up-

holding the rights of the inventor upon protests against final allowance of the patent. This is only conditional up to the publication as prescribed by the German Law analogue to our publishing of applications for trade marks.

The one point alluded to above represents a shortcoming peculiar to both the American and German Patent Practice. Our information indicates that German inventors have to suffer just as much from certain Patent Office proceedings as the American inventor. The rock on which the hopes of many an inventor with a meritorious proposition are wrecked is the examiner's decision:—*Lack of novelty, or lack of invention.* Such a decision dooms nearly any application to an untimely death, for on appeal the examiner's opinion is usually sustained.

It has recently been amply shown that the examiners and the staff of the U. S. Patent Office are altogether too overburdened with work to make a very far-reaching search of the prior art, and that they very often, after finding some prior patents, give the same such a broad interpretation as to negative a new application. These shortcomings have been very heavily felt by the American industry for it happens relatively often that a patent is denied because in view of some former often irrelevant arts the examiner denies the application the dignity of invention. Just such "microscopical" inventions, for which protection by patent letters was denied or could be obtained only under great difficulties, have later on become splendid industrial successes. We hope that such inventions may find salvation with the future U. S. Patent Court of Appeals, where any party aggrieved by adverse decisions may have due redress.

Things are similar in Germany. The very same trouble in overcoming the resistance of the examiner to applications apparently bare of inventions was lately the matter of many and hard complaints at the meeting of the Berlin Section of the Association of German Chemists. We learn from the *Zeitschrift fuer angewandte Chemie* (March 29, 1912, pages 636–7) that several speakers severely criticized the Examiners of the German Patent Office especially for reading too much between the lines and for incorporating into literature certain information from a new application, thereby interpreting said literature in a broad sense which never would be done by an unprejudiced reader without knowledge of the new application. The practice of combining several quotations from literature by a certain order of reasoning in order to prove existence of the subject matter previous to the new application was also clearly pointed out. Much complicated reasoning and quibbling is often resorted to which more than anything else is sufficient proof of invention in behalf of applicant. Some other complainants pointed out that the requirements of the German Patent Office for "originality" of invention are too far reacting in view of the present high development of industry. For this reason most inventors can only submit improvements of the present art, such improvements being entitled to protection if they bring the art nearer to the goal of perfection. A high official of the German Patent Office was present at this meeting and was in a rather tight place for the tone of the complaints was rather bitter.

The same complaints must be made against the American Examiner. It may be said in behalf of both the American and German Patent Examiners that the severe standpoint in adjudging new applications is taken with the best intentions for protecting the interests of older patentees but the echo we hear from abroad is another proof that this shortcoming is really existing to the chagrin of inventors and that we should strive for proper means to repair a too broad interpretation of the prior art as detrimental to the justifiable claims of an inventor.

Suggestions to this effect were lately made in Germany, and it is interesting to note that one of them consisted in recommending the provision of funds to send every Examiner and the Sub-Examiners of the staff once in two to three years on a six weeks' tour for inspecting industrial works. He would then gain thorough information about the latest developments of industry, and get a better view on the exigencies of business by making the personal acquaintance of the men who keep things moving.

REPORT OF THE DELEGATE TO THE JOINT CONFERENCE ON THE PATENT SYSTEM.

The Committee delegated to attend the conference on the Patent System held in Washington, April 15th and 16th, attended the conference and advocated the appointment of a Board of Experts to which all matters relating to Patent Legislation should be referred for report before action is taken by Congress in formulating and enacting changes in the present laws governing the issuance, scope and regulation of patents.

After consideration and discussion of the various bills now before Congress the following report was agreed upon by the Informal Joint Conference.

Informal Joint Conference.

At a meeting of representatives from the following associations held at Washington on the 15th and 16th of April, 1912, over forty bills affecting the patent system of the United States were considered to such extent as time permitted. Many of these bills are obviously of a radical character—aimed at fundamental principles of the patent system—and others deal with such complicated matters as Patent Office procedure and practice.

After extended discussion, in view of the importance of careful consideration of the said bills, to the end that the patent system of the United States, to which in so large a measure our industrial prosperity is due, may not be unduly affected, it was unanimously resolved that the representatives of the several associations there represented agree to recommend to their respective associations:

(1) That the committee of Congress be respectfully urged to defer action on said bills until the associations represented at the conference, and the public generally, have had ample opportunity to study the bills and determine what may be the full effect of the changes contemplated by them.

(2) That a recommendation be made to the respective associations to appoint members of a joint Standing Committee with power, subject to the call of the Chairman of the Patent Law Association of Washington, to study the pending bills and the whole patent situation and adopt means for such action as may appear expedient.

Subsequently, the conference, to carry out the purpose of the concluding clause of the preceding resolution, unanimously adopted the following:

RESOLVED: "That the associations here represented, and such associations as shall be hereafter added thereto, shall appoint, each, three delegates, each association to have one vote, and that a committee, consisting of Mr. Rogers, Dr. Baekeland and Mr. Mershon, shall be appointed, which may add at its discretion associations and members to meet in future joint conferences."

American Chemical Society.
American Electrochemical Society.
American Institute of Electrical Engineers.
American Institute of Mining Engineers.
American Society of Mechanical Engineers.
Chemists' Club of New York.
Institute of Chemical Engineers.
Inventors' Guild.
Patent Law Association of Chicago.
Patent Law Association of Washington.

NEW YORK COUNTY LAWYERS' ASSOCIATION AND NON-RESIDENT MEMBERS PATENT LAW ASSOCIATION OF WASHINGTON.

The various organizations were represented as follows:

AMERICAN CHEMICAL SOCIETY.—Clinton P. Townsend, Washington; Professor Charles E. Munroe, Washington.

AMERICAN ELECTROCHEMICAL SOCIETY.—Dr. L. H. Backeland, Yonkers, N. Y.; A. B. Marvin, Marquette Bldg., Chicago.

AMERICAN INSTITUTE OF ELECTRICAL ENGINEERS.—A. W. Berresford, Milwaukee; F. P. Fish, Boston; Dugald C. Jackson, Boston; M. I. Pupin, New York.

AMERICAN INSTITUTE MINING ENGINEERS.—Capt. A. F. Lucas, Washington.

AMERICAN SOCIETY OF MECHANICAL ENGINEERS.—W. H. Blauvelt, Syracuse, N. Y.; B. F. Wood, Altoona, Pa.

CHEMISTS' CLUB OF NEW YORK.—Carleton Ellis, New York.

INSTITUTE OF CHEMICAL ENGINEERS.—Dr. Wm. M. Grosvenor, New York; Maximilian Toch, New York.

INVENTORS' GUILD.—Ralph D. Mershon, New York; H. Ward Leonard, New York.

PATENT LAW ASSOCIATION OF WASHINGTON.—Walter F. Rogers, Washington; William W. Dodge, Washington.

PATENT LAW ASSOCIATION OF CHICAGO.—Thos. F. Sheridan, Chicago.

NEW YORK COUNTY LAWYERS' ASSOCIATION AND NON-RESIDENT MEMBERS PATENT LAW ASSOCIATION OF WASHINGTON.—Wm. H. Kenyon, New York; Alfred W. Kiddle, New York; E. W. Bradford, Washington and Indianapolis; Robert C. Mitchell, New York; Odin Roberts, Boston; George O. G. Coale, Boston.

Yours very truly,

CHARLES E. MUNROE, *Delegate.*

REPORT OF THE COMMITTEE ON QUANTITATIVE METHODS.

During the past six months your committee has done some work on volumetric and gravimetric methods of assay for the various zinc salts official in the Pharmacopoeia, and begs to submit herewith a report of this work together with a bibliography of various articles dealing with the quantitative estimation of zinc which have appeared from 1890 to the present date.

The results of co-operative work on zinc assays follow and comments of the various members of the committee are appended to this report.

The gravimetric method was referred to in report of July last and is the well-known Ammonium Phosphate Precipitation Method. The volumetric method is that published by E. Rupp, *Chemiker Zeitung*, **33**, 3 (1909), which is as follows:

"Prepare a solution of the zinc salt containing the equivalent of 0.1 gram of metallic zinc, using dilute sulphuric acid to make the solution if necessary, as with zinc oxide, and subsequently exactly neutralizing the solution with $N/1$ NaOH. This solution should measure about 10 cc.

"Dilute exactly 20 cc. of approximately 5 per cent. solution potassium ferrocyanide to 50 cc. with water and dissolve in this 5 grams of potassium sodium tartrate. To this solution add the zinc solution and let stand for 30 minutes, in order that the zinc ferrocyanide as precipitated may be transformed into potassium zinc ferrocyanide.

"Now add 30 cc. of $N/10$ I and let stand for one hour whereby the excess ferrocyanide is converted into ferricyanide quantitatively. Titrate the excess $N/10$ I with $N/10$ sodium thiosulphate.

"At the same time a blank test may be run in exactly the same manner, omitting the zinc solution so as to determine the iodine value of the potassium ferrocyanide solution. The difference between the amount of iodine consumed as an oxidizing agent in the blank and that consumed in the actual assay corresponds to the quantity of zinc present:

$$3Zn = 2I.$$

0.00981 gm. Zn = 1 cc. $N/10$ I."

ZINC ESTIMATIONS.

Mr. Briggs

Volumetric.		Gravimetric.	
Zinc oxide. Per cent.	Zinc phenolsulphonate. Per cent.	Zinc oxide. Per cent.	Zinc phenolsulphonate. Per cent.
97.54–97.54	103.12–102.14	98.9	99.3
99.84–101.29		98.2	99.2
Av. 99.05	Av. 102.63	Av. 98.55	Av. 99.15
By using more for assay.			
96.5 – 96.9	91.8 – 92.6		
Av. 96.7	Av. 92.2		

Mr. Engelhardt.

Standing 1 hr. with $N/10$ I. Per cent.		As NH_4ZnPO_4. Per cent.	As NH_4ZnPO_4. Per cent.
100.5 –104.8	No proper results could be obtained with this slt.	101.2 –100.9	101.6 –101.6
101.7		100.1	101.6 –102.1
Av. 102.33		Av. 100.73	Av. 101.7
Standing over night.		As $Zn_2P_2O_7$. Per cent.	As $Zn_2P_2O_7$. Per cent.
97.9 – 98.2		99.5 – 99.9	100.01–100.03
		99.6	100.05–100.2
Av. 98.05		Av. 99.73	Av. 100.08

Mr. Brown.

Per cent.		As NH_4ZnPO_4. Per cent.	As NH_4ZnPO_4. Per cent.
92.54– 97.13	No satisfactory results.	99.99–100.29	100.4 –100.71
96.53– 99.4		99.86–100.12	98.16– 97.73
100.53– 97.89			
98.95			
Av. 97.56		Av. 100.06	Av. 99.25
		As $Zn_2P_2O_7$. Per cent.	As $Zn_2P_2O_7$. Per cent.
		99.51–100.03	100.09–100.45
		99.40– 99.60	97.12– 96.68
		Av. 99.63	Av. 98.58

Mr. Taylor.

Per cent.		As NH_4ZnPO_4. Per cent.	
101.1 – 98.58	No reliable results obtained.	100.73–100.95	
98.77– 98.58		....	
Av. 99.23		Av. 100.88	
		As $Zn_2P_2O_7$. Per cent.	As $Zn_2P_2O_7$. Per cent.
		99.95–100.16	99.34–99.18
		Av. 100.05	Av. 99.34–99.04

MR. BRIGGS: "The Gravimetric Method is more accurate and preferable."

MR. ENGELHARDT:

As to the Volumetric Method, says: "This method, although somewhat shorter than the Precipitation Method, gives unreliable results when carried out according to instructions."

As to the Gravimetric Method:

"This method which is used exclusively in the laboratory here works very well. I prefer estimating the zinc as pyrophosphate, although if the precipitate of the ammonium zinc phosphate is washed thoroughly as directed, the results are

too high, probably due to the presence of ammonium phosphate.

"The high results obtained with the zinc phenolsulphonate may be due to the salt having lost some of its water of crystallization."

MR. BROWN: "The Volumetric Method does not appear to be reliable. This objection may be removed by a further study of the method, allowing more time for the reaction between the iodine and ferrocyanide to take place, also to determine whether the reaction proceeds better in a neutral solution slightly acid or strongly so, etc."

"The Gravimetric Method: "It appears to be very satisfactory in point of accuracy and speed. However, I think the amount of wash water called for in the method is entirely too much as there are no difficultly soluble salts to wash out and such a large volume of wash water dissolves an unnecessarily large amount of the precipitate.

"There appears to be a slight loss of zinc on ignition to the pyrophosphate. I think more work should be done along this line to determine whether this is true, also to determine whether more accurate results are to be obtained by weighing as the zinc ammonium phosphate or as the pyrophosphate."

MR. TAYLOR: "The Volumetric Method gives fair results with zinc oxide but requires a larger sample than given in the assay processes used to be at all sure of results. Four assays by this method on the phenolsulphonate give results about one-fourth of the theoretical for no apparent reason. The method is entirely unsatisfactory for this salt, and because of the fact that the least variation in the results makes a considerable difference in the percentage of the zinc salts found, the method is not desirable."

"The Gravimetric Method is almost as rapid and decidedly more accurate than the Volumetric Method, and it seems preferable to estimate directly as pyrophosphate. The entire assay can be run within a period of three hours, and on the whole it seems that this is the most desirable method for the assay of all zinc salts."

The high percentage obtained on the zinc oxide by most of the members of the committee is probably due to the distinct trace of some calcium salt, evidently the carbonate present in the zinc oxide sample which was sent out. This, of course, does not show in the solubility of the zinc oxide unless sulphuric acid is used for its solution as directed.

The chairman of the committee would suggest for the consideration of the division during the next six months or year, if necessary, a very careful survey and testing out of methods of assay for capsicum and cantharides be taken up by the committee as two substances of considerable interest for which there is neither a standard in the Pharmacopoeia nor a method assay. If, however, the division prefers the committee to continue in exactly the manner that has been done on the zinc and mercury salts, we shall be glad to follow out these instructions.

Respectfully submitted,

LINWOOD A. BROWN,
C. H. BRIGGS,
H. ENGELHARDT,
L. D. HAVENHILL,
B. L. MURRAY,
A. P. SY,
FRANK O. TAYLOR, *Chairman.*

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THE TECHNICAL ANALYSIS OF BRASS AND THE NON-FERROUS ALLOYS: AUTHOR'S NOTE.

Editor of the Journal of Industrial and Engineering Chemistry:

My attention has been directed to a review of "The Technical Analysis of Brass and the Non-ferrous Alloys," which appeared in the March number of your excellent Journal. This review contains so many misleading statements and shows evidence of such careless reviewing that I am forced to call attention to the same.

First.—In discussing the first part of the book, in which it is stated that "it is liable to confuse the reader when he finds two entirely different analysis of, for instance, Delta metal," I am unable to see how any reader could be confused, in view of the fact that one Delta metal is placed in Table No. 1, dealing with bearing metals, while the other Delta metal is placed in Table No. 3, under foundry and rolling mill alloys. One would not be likely to take a metal containing 92.4 per cent. copper to be one and the same with an alloy containing 55.94 per cent. of copper.

Second.—The reviewer states: "The authors do not mention the fact that precipitates of the hydroxides, especially if precipitated by ammonia, are almost certain to contain silica, and often phosphoric acid, in sufficient quantity to cause serious error." In this connection, the reviewer evidently speaks from the standpoint of iron and steel, as brass and the general run of non-ferrous alloys contain such minute quantities of silica, that they would have no effect on the accuracy of the determination.

Third.—The statement, "under lead they advise washing the precipitate of sulphate with a mixture of water, sulphuric acid and alcohol; this is apt to give high results, as few sulphates are readily soluble in alcohol. The precipitate should first be washed free from sulphates with dilute sulphuric acid, and after this has drained off, with alcohol." If these directions were carried out, lead results would be low, as lead sulphate is soluble in dilute sulphuric acid, and it is for this very reason that the alcohol is added to render the lead sulphate insoluble, and it has been repeatedly shown that the solubility of the copper and zinc sulphates, after having been dissolved in hot water, are not effected by the amount of alcohol used in the washing solution as recommended.

Fourth.—"For the volumetric determination of manganese, they give the old Williams method, apparently not knowing that it has been shown that it is incapable of giving correct results as the precipitate is not MnO_2 but a lower oxide. They also give the method of Metzger and McCrackan but do not give the Volhard method which most analysts have found the simplest, quickest and most accurate." While the Volhard method, it is true, may be superior to the Williams method for iron and steel, for the analysis of brass and the non-ferrous alloys, the combined Williams and Ford method, as described on page 103, has been found to be vastly superior to the Volhard method. Two of the largest brass laboratories in the country are using the Williams and Ford method in preference to the Volhard, after having made a long series of tests with both methods.

Fifth.—"They advise the use of aluminum for the reduction of iron but do not mention that commercial aluminum usually contains enough iron to cause a serious error." More careful reviewing would have made it evident that the authors specifically mention this fact under Iron, page 83, line 1: "To the solution in the six-oz. flask, add 2 grams of pure aluminum sheet or drillings. Weigh this fairly accurately, as *all aluminum contains a little iron which must be deducted from the total iron found*," and, again, on page 84, line 8: "A small correction must be applied to the burette reading to allow for the amount of permanganate used to produce a pink tint in a blank solution containing the same amount of aluminum and the same amount of acids and water used but without any iron wire." "Dissolve two grams of aluminum, etc.;" "Subtract the correction thus obtained from every burette reading."

Sixth.—"In the description of the volumetric method for zinc, they do not lay enough stress on the necessity of keeping all conditions uniform. Variations in the temperature, acidity, and amount of ammonium chloride present, all affect the end point." In this connection, it did not seem necessary to burden the reader with all of Waring's different experiments and results connected with the temperature, acidity, and amount of ammonium chloride present, especially as the amounts of hydrochloric acid, ammonium chloride and temperature, as given on pages 141 to 145, inc., are exactly the same as the conditions given by Waring to insure accurate results after he had investigated the effect of temperature, acidity, and amounts of ammonium chloride on the end point.

It is to be regretted that this book could not have been reviewed with more care.

WM. B. PRICE.

SCOVILL MANUFACTURING CO.
May, 1912.

VOLATILITY OF METALS OF THE PLATINUM GROUP.

During the reading of a paper on "The Volatility of Metals of the Platinum Group," read before the members of the British Royal Society in March, Sir William Crookes narrated some observations which indicate that platinum is not so entirely fixed at temperatures well below its melting point as has been universally accepted by chemists and physicists.

In using an electric furnace consisting of a coil of platinum ribbon contained in a porcelain tube he found that in time the ribbon grew thinner till it melted at the weakest part. When that happened he noticed that the porcelain tube was coated with a fine dust of beautifully formed crystals of brilliant metallic luster, which on analysis proved to be platinum. It therefore seemed of interest to subject a platinum crucible to a temperature approaching that to which the platinum resistance coil had been exposed. A crucible was heated to 1,300° C. in the electric furnace for 30 hours when the loss of weight amounted to 0.245 per cent. Palladium, treated in the same way, lost 0.745 per cent. in 30 hours. An iridium crucible lost over 7 per cent. in weight after 22 hours at 1,300°, and at greater heat, loss of weight for equal periods of time was proportional to temperature. After this severe treatment, the crucible, which had taken on a crystalline appearance over the whole surface when the series commenced, began to show disintegration along its edges and pieces began to crumble when touched with the forceps. With rhodium, a metal intermediate in fusibility between platinum and iridium, the loss in 30 hours was 0.13 per cent., not far from that of platinum.

Experiments were then made at 900° by heating the metals in a flame of a good Méker burner. Platinum and rhodium after heating for 20 hours showed no loss of weight, but palladium in 10 hours lost 0.0919, and iridium in 20 hours lost 0.091 per cent.

In an experiment to see whether iridium would volatilize at a high temperature in a vacuum, a fused silica tube had a bulb blown on the end. In the bulb were put 27.619 grains of clean iridium; the other end of the silica tube was drawn out for connecting with the pump and sealing. It was exhausted to a high vacuum and heated to near redness along its whole length till all moisture and occluded gases had been removed; it was then sealed off, and placed in the furnace in such a position that the iridium would be at the point of greatest heat. The bulb was kept at a temperature of 1,300° for 30 hours. On examining the silica tube when cold it was seen that the long continued high temperature had caused the bulb and the upper part of the tube to devitrify and become white and translucent and that it had an irregular black deposit on the lower part, which proved to be metallic iridium.

LONDON, March 13, 1912.

CHEMISTRY AND THE LITHOGRAPHIC INDUSTRY.

Editor Journal of Industrial and Engineering Chemistry:

The article in the January number by Mr. W. H. Watkins strongly appealed to the writer, who may be classed as a chemist in one of the industries in which "there are almost no chemists." A few years ago my attention was directed to the lithographic industry as one involving chemical processes to a large extent. These processes, almost without exception, had developed by rule-of-thumb methods and were entirely without technical control. A given operation would be successful one day and unsuccessful the next, depending on the "luck" of the operator.

After carrying on research work for some time to convince myself that the rule-of-thumb man was not always correct in his methods and deductions, I laid some of the laboratory results before a lithographic firm for its consideration. The work of demonstrating the advantages of chemical control in this particular line of manufacture, although somewhat slow at the beginning, was eventually convincing. A laboratory was installed in the plant, and actual work begun. Changes were made in the processes one after another. Not only in the testing of raw materials but more especially in modifying some of the time-honored practices, the work met with considerable opposition from the "practical" man who had done it the old way for so many years. The attitude of some of the men concerned in these changes was well described by Mr. A. D. Little in his recent lecture on "The Earning Power of Chemistry." They certainly took no pains to conceal their "militant skepticism." To-day this laboratory, with its system of control, is an integral part of the factory and is regarded as one of the essential departments.

It is of the utmost importance in work of this character for the chemist to familiarize himself as rapidly and as completely as possible with the details of the manufacturing processes. While often wrong from the standpoint of the theory-shrouded technical graduate, the practical man may be nearly correct as far as he goes, but the chemist, or chemical engineer, can investigate the problem more thoroughly and by properly classifying the data at his disposal obtain the desired results. The work of both these men can be materially lightened by consistent coöperation. In the lithographic industry, as well as in industries where chemists are more generally employed, the chemist should bear in mind that in addition to his more specific duties he must endeavor to become an efficiency expert. This feature of his work is sure to attract the attention of the manager of the varnish, ink, or paint works, as the case may be, whereas the more technical details would pass unnoticed. Whether it be the mere routine testing of finished products or the perfection of methods for the profitable utilization of waste, the progressive manufacturer is not going to rely upon "the fellow who doesn't know any better." He is realizing more each year the need for technically trained men. Men trained in chemistry should force their way into *new* industries if this "century of chemistry" is to be realized. To use an expression

of Prof. Wm. Ostwald, it behooves us to "put more brains into the goods" and into a greater variety of goods, if the chemist's hopes are to end in fruition. B. P. JAGGARD.

SAN FRANCISCO.

CONTAMINATION OF LABORATORY SAMPLES BY IRON DERIVED FROM CRUSHING MACHINERY.

By VICTOR LENHER.

The article by George A. James on the "Contamination of Laboratory Samples by Iron Derived from Crushing Machinery" in *The Chemical Engineer*, 14, 380, Sept., 1911, calls attention to the too often neglected fact that in the preparation of samples for analysis the crushing or grinding apparatus employed may introduce material in such kind and quantity as would render the analysis worthless. Dr. Hillebrand, in *Bull.* 422, U. S. Geol. Survey, p. 50, lays stress on this point. Too much emphasis cannot be laid on the choice of grinding apparatus used in the preparation of samples for analysis. Recently a series of samples of quartzite were collected by the writer for analysis. Inasmuch as the quartzite beds, from which the samples were taken, were being valued for the purpose of being used in the manufacture of silica brick, it was desirable to obtain an accurate determination of the content of silica and particularly of iron.

Sample No.	Metallic iron introduced from crusher. Per cent.	Iron content of quartzite. Per cent.
1	2.92	0.49
2	2.74	0.49
3	2.73	0.23
4	2.61	0.63
5	2.82	0.25
6	2.59	0.29
7	1.86	0.55
8	2.46	0.16
9	2.65	0.75
10	2.67	0.12
11	2.81	0.16
12	1.87	0.06
13	1.98	0.20
14	2.01	0.68
15	2.62	0.11

The samples on being brought to the laboratory consisted of chips of the rocks, approximating in size $^3/_4$ inch square by $^1/_4$ inch thick. After being broken somewhat smaller by means of a hammer, they were reduced in a Braun crusher to pass a 120-mesh screen. The material in the original beds is of a light pinkish cast, while the powdered material was distinctly gray. Tests by the magnet revealed the presence of metallic iron in the powdered quartzite, but owing to the fine state of division of the powder, it was found to be impossible to satisfactorily remove the iron by mean of the magnet.

Treatment of the powder with dilute sulfuric acid and subsequent analysis of the remaining quartzite is shown in the accompanying table.

The variation in the amount of metallic iron abraded from the crusher is, of course, dependent on the length of time of crushing.

It is interesting to note in connection with the above results that a similar set of samples were sent to one of the largest iron laboratories in the northwest, and reports were made showing an apparent iron content of the quartzite to be from 1.42–2.97 per cent. iron.

It has been the frequent experience of the writer in the analysis of igneous and metamorphic rocks to find the sample contaminated by iron from the bucking board, crusher, or such grinder as may have been used in reducing the sample. As a rule this metallic iron can be removed and at the same time determined by treatment with dilute sulfuric acid and subsequent titration with permanganate. As a matter of fact, the more common material which will materially abrade iron or steel in crushing is not appreciably attacked by dilute sulfuric acid during the few minutes contact that is requisite to dissolve the finely divided iron. On the other hand, the general type of ores and products, which will themselves lose part or all of their iron to dilute sulfuric, will not appreciably abrade steel from the types of grinding apparatus on the market.

It cannot be too strongly emphasized, however, that the chemist is called upon to report on the constituents sought for, and when the common danger of contamination in the preparation of his sample presents itself, great care must be exercised to eliminate such errors.

UNIVERSITY OF WISCONSIN,
MADISON.

COMBATING MINERS' DISEASES.

An arrangement has been made with the Public Health and Marine Hospital Service by which one or more surgeons connected with that service will carry on jointly for that service and for the Bureau of Mines investigations looking to the improvement of mine conditions. These inquiries and investigations have already shown the prevalence of tuberculosis and hookworm as miners' diseases in a number of different localities in the United States. It is important that this work should be extended more rapidly, because of the fact that the health conditions, as well as the risk of accidents, may be influenced by conditions susceptible of easy improvement. Furthermore, the large and continuous influx of foreigners into the mining regions of the United States will bring to an increasing extent the hookworm and other diseases that abound in mines in parts of certain European countries.

Various questions that concern the health of workers in mines, quarries, and metallurgical plants can not be answered finally without investigations and inquiries that are national in scope. Among such questions are the most efficient methods of preventing the diseases peculiar to certain industries, the most effective sanitary precautions to be observed in and about coal mines and metal mines, and the relative healthfulness of occupations pertaining to mining and metallurgical industries. The investigations and inquiries that are essential to the gathering of reliable information on these questions can be undertaken by the Bureau of Mines, in connection with its collection of accident statistics, in a prompt and efficient manner and at minimum expense.

BOOK REVIEWS

Strength of Materials. By S. E. SLOCUM AND E. L. HANCOCK. New York. Ginn & Co. Revised edition. 1911. XXXVI + 372 pp. Price, $3.00.

The present volume is a revised edition of a previous publication appearing in 1906. It consists of two parts dealing with Mechanics of Materials, Part I, 262 pages, and Physical Properties of Materials, Part II, 110 pages.

The subject matter of Part I relates to the elastic properties of materials, the evaluation of and relation between the elastic constants, stress distribution in straight and curved beams, under different systems of loading and support, columns and struts, shafting, thick and thin cylinders, flat plates, springs, hooks, arches of concrete and masonry, foundations and retaining walls. A most rigid and satisfactory analysis is applied

to each of the above cases, and comparisons with less rigid analyses are given, to the end that a study of the text will enable one to clearly understand the fundamental and complex relations of stress and strains in a wide range of formulative conditions. A number of problems at the close of each chapter are helpful to an appreciation of the extent to which the theories are applicable.

Part II relating to the physical properties of materials is given to the reports of experiments on engineering materials of which are selected: Iron and steel of varying compositions and heat treatments, lime, cement and concrete, brick and building stone, timber, rope, wire, leather and rubber belting. From these experiments are derived the constants and relations necessary to a quantitative treatment of the preceding part of the text.

Throughout the whole text many references to original sources and more extensive treatments are given.

The notation is very consistent. The printing, illustrations and binding are all that could be desired.

WALTER RAUTENSTRAUCH.

Fertilizer and Fertilizer Hints. By JAMES EDWARD HALLIGAN. 155 pages. 11 illustrations. The Chemical Publishing Co. 1911. Price, $1.25.

This book is an abridged edition of the author's "Soil Fertility and Fertilizers." The author has succeeded well in his endeavors to produce a volume which will be within the reach of the farmer, student or other persons interested in the subject of fertilizers.

The different subjects are only briefly discussed and yet by reading this volume one can get a very clear understanding of the usually accepted views concerning soil fertility and the composition and functions of fertilizers.

The work is divided into fifteen chapters as follows:

Chapter I: Chemical Elements needed by Plants and the Composition of Plants.

Chapter II: The Fertility of the Soil.

Chapter III: Maintaining Soil Fertility.

Chapter IV: Farm Manures.

Chapter V: High-grade Nitrogenous Materials.

Chapter VI: Low-grade Nitrogenous Materials and Functions of Nitrogen.

Chapter VII: Phosphates.

Chapter VIII: Superphosphates and Effect of Phosphoric Acid.

Chapter IX: Potash Fertilizers.

Chapter X: Miscellaneous Fertilizer Materials.

Chapter XI: Lime, Gypsum and Green Manures.

Chapter XII: Commercial Fertilizers.

Chapter XIII: Valuation of Fertilizers.

Chapter XIV: Home Mixtures.

Chapter XV: A Few Remarks about Fertilizers.

In addition to the subject matter indicated by the index, there are many tabulations giving valuable data with reference to the composition of different farm products, etc.

The book is a useful one as a brief general treatise on the subject and is well adapted for the purpose which was intended.

F. B. CARPENTER.

Die Chemie der Cellulose with Particular Reference to the Textile and Cellulose Industries. CARL G. SCHWALBE, Ph.D., Berlin. 1911. 2nd half, 8vo. 392 pp., with preface and index to complete work.

The second half upholds the excellent standard of the first. It contains the consideration of the esters of cellulose, probably not as much in detail as the author's intimate knowledge of the subject might lead one to expect, but undoubtedly as comprehensively as the space prescribed to it permits.

The general consideration of cotton cellulose (I) is concluded by reference to its decompositions, its constitution and its colloidal character. Under II is considered natural compound celluloses, the ligno-celluloses, the pectocelluloses, mucocelluloses, cuto- and adipocelluloses, and peat and humus. Section III treats of the technical manipulation of the plant sources of compound celluloses, subdividing the subject into ligno-celluloses and into pectocelluloses; and Section IV deals with different forms of cellulose so prepared. Under Section V is briefly described and considered mercerization, artificial silk manufacture, rag cooking, and manufacture of parchment and vulcanized fiber. The concluding section (VI) is on analytic methods of cellulose chemistry and is subdivided into qualitative and quantitative analysis.

The entire work is a distinctly useful contribution to the literature on cellulose and its chemistry. H. S. MORK.

Chemiker Kalender. By DR. RUDOLF BIEDERMANN. Thirty-third year. In two volumes. Vol. 1, pp. 400; Vol. 2, pp. 641. Berlin: Julius Springer. 1912. Price: Cloth, M. 4.40; leather, M. 5.40.

The universally-known Chemiker Kalender now in its thirty-third year appears for 1912 with the number of pages somewhat augmented and with the very distinct advantage of having both volumes bound. Instead of naming the second part of the work "Beilage" as in former years it is now simply Volume 2 of the Chemiker Kalender, which is quite satisfactory. Vol. 1 now has 400 pages instead of 389 as in 1911 and Vol. 2 has 641 pages instead of 608. The regular increase from year to year indicates that this most useful work is constantly in a state of active revision and is not permitted by its author and editor to fall behind the times. A useful extension for future years would be the addition of more equilibrium diagrams and tables for water-salt solutions to replace in part or extend the present solubility tables in Vol. 1. W. D. RICHARDSON.

The Manufacture of Varnishes, and Kindred Industries. By J. G. MCINTOSH. Three vols., 1904, 1908, 1911. pp. 153, 209, 482. Scott, Greenwood & Co. Price, Vol. III, $4.50.

This book is said to be based on and to include Livache's "Drying Oils and Varnishes"; in fact, McIntosh originally published what was practically a translation of Livache, a book of no great interest to the English-speaking public; but the present book is by McIntosh: readable, more than fairly accurate, and full of good sense and practical knowledge.

Vol. I is on linseed oil; from a technical standpoint it is not equal to Ennis' book though, as it shows English practice instead of American, it may be regarded as supplementary to that; but as a chemical book it is by far the best on the subject.

The common and commercially important (at least in America) method of bleaching oil with Fuller's earth is nowhere mentioned, nor the "break" of raw oil, which is one reason for refining; but it gives much historical matter and European practice up to the date of publication, as well as considerable analytical and other chemical data.

Vol. II is on oleo-resinous varnishes, and contains especially much apparently accurate information about amber and copals, not to be found elsewhere, so far as the present writer's knowledge extends; it includes recent German and French investigations. The part on varnish-making contains much good historical matter, and European experiments.

Vol. III is on spirit varnishes, and is complete and up to date. It has a large amount of data on resins as well as solvents, and is the most satisfactory treatise yet published on the subject. It is better than either of the other volumes, because larger and fuller. A. H. SABIN.

Technical Methods of Chemical Analysis. By DR. GEORGE LUNGE and many others. English translation by Dr. Charles A. Keane, with a large number of collaborators. Vol. II in two parts. Part I, pp. xxvii and 610; Part II, pp. xii and

611 to 1252. New York: D. Van Nostrand & Co. 1911. Net price, $18.00 set. Not sold separately.

Analytical and technical chemists will welcome this English translation of the latest (6th) edition of Dr. Lunge's well-known work. The earlier German editions of Dr. Lunge's "Technical Methods" have been in use by chemists so long that it is unnecessary to go into the merits of this excellent work at this time, except to indicate its scope and list the material embodied in this volume.

To quote from the translator's preface, "The sections comprised in this second volume of the English edition are included in the second and third volumes of the new German edition which is being issued in four volumes." Again, "The section on Organic Dyes from Vol. IV of the German edition has been included in this volume, as it forms a suitable sequel to the section on Coal Tar."

The topics covered in Part I are: Iron, Metals other than Iron (including 22 of the more important metals), Metallic Salts, Artificial Manures, Feeding Stuffs, Explosives, Matches and Fireworks, Calcium Carbide and Acetylene.

In Part II are found: Illuminating Gas and Ammonia, Coal Tar, Synthetic Organic Dyes, and Naturally-occurring Organic Dyestuffs. Numerous references are given throughout the book, and at the end of each section, under the heading "Literature," is a well selected list of the important books dealing with the subject.

It is impossible, even in a work of this size, to give all of the methods of analysis which might be considered as good, and the authors are to be complimented on the selections they have made. The subject matter has been brought up to date remarkably well.

The appearance of this work in English will undoubtedly greatly extend its field of usefulness, and give it the recognition so fully deserves. F. J. METZGER.

Cocoa and Chocolate, Their Chemistry and Manufacture. By R. WHYMPER. 327 pages. P. Blakiston's Son & Co., Philadelphia. Price, $5.00 net.

The present volume, divided in 3 parts, describes the agricultural, technical and chemical sides of the cocoa and chocolate industry.

In the first part of the book the history and development of the industry are reviewed, the botany and nomenclature discussed, and the agricultural operations of planting, pruning, picking, fermenting, and preparing the cocoa beans described.

In the second division of the work the manufacture of chocolate and cocoa powders from the raw beans is taken up. The operations of cleaning, roasting, nibbing, milling, etc., are described, and details given for the manufacture of plain, milk, and fancy chocolates and numerous cocoa preparations.

In the third part of the volume a comprehensive survey is taken of the composition of cacao and its preparations; methods for their analysis are described. The chemical data are very complete and as the author states: "For the first time the chemical composition of cacao has been traced from the fresh bean through various stages of manufacture, so that the changes which occur during fermentation, drying, roasting, etc., may be followed. The most recent methods of analysis have been discussed, and the author has only recommended those which he himself has found to give accurate and consistent results."

The author limits the term cacao to the raw material and cocoa to the powder manufactured from the nibs. The confusion which so frequently attends the use of these two terms is thus largely avoided, although it seems that the distinction cannot always be sharply drawn; the coloring substance of chocolate for example is listed in the index both as cacao-red and cocoa red.

The new volume is well printed and splendidly illustrated with 12 full page photographs giving views of the agriculture of cacao in Trinidad. Other cuts show machinery, microscopical sections of pure and adulterated cocoa, etc. A useful appendix gives the provisional definitions of standards of cacao and its preparations and a very complete bibliography.

Of the numerous works which describe the manufacture and chemistry of foodstuffs, Whymper's cocoa and chocolate is one of the best which has come to our notice.

C. A. BROWNE.

A Manual of Fire Assaying. By CHAS. H. FULTON. Second edition. pp. xvi + 209. McGraw-Hill Book Co., New York. Price, $2.00.

The second edition of this book retains all the commendable features of the previous edition, and is improved by the elimination or correction of questionable matter and the addition of new material.

The chapter on furnaces deals with the various types to date, their advantages, application, and the cost of operation under definite conditions.

There is little change in the chapter on reagents except for a more complete discussion of the action of boric acid and borates and somewhat greater attention to the cyanides.

The chapter on sampling has been slightly modified, but could stand considerable improvement to be truly useful to the student. However, this chapter and the book as a whole contain sufficient of the best references to make up for anything lacking in the text.

The subject of reduction and oxidation is extensively considered, and the points that affect the amount of lead reduced well discussed. In this connection it is surprising that the temperature effect was not brought out.

Slags have been considered from the silicate basis of the metallurgist. This method has been adopted by other writers but its value is doubtful. The author states that slags are solutions; they are more than this, in the fluid state they are electrolytes. He also states that the different bases require different silicate degrees for the best results. It is a fact that certain charges for Fe_2O_3 which will give good slags, if calculated for MnO_2, would be absolutely worthless and unsatisfactory for $CaCO_3$. There is positively no chemical relation, that we know, by which we can calculate the required silica irrespective of the base. From these facts it is difficult to see wherein this method of giving charges is scientific or what benefits are to be derived from a series of calculations, when the empirical method of stating directly the charge for a given mineral or compound is much simpler and makes no ambiguous pretentions.

The subject of cupellation has been handled in a masterly manner, and considerable new matter has been added from the author's investigations. All phenomena have been very carefully noted with their cause and effect. There are but two points on this subject open to criticism: (1) the failure of PbO to volatilize being assigned the cause of low temperature freezing (generally this is due to the cupel becoming too cool to absorb litharge); (2) that it is necessary to remove cupels from the furnace directly the beads have finished. As cupellation is properly finished with a furnace temperature below the melting point of silver, the bead sets shortly after the lead is removed, and as silver is not readily sublimed immediate removal is not necessary. This has been proved by test.

Under the headings of the assay of ores containing impurities and special methods of assay, various schemes of assay and the treatment of impurities are well considered. The latest methods and experiences are treated and the underlying principles explained.

The book as a whole is the most complete and reliable on the subject, but it could be more conveniently arranged. Subject matter directly related is treated under different heads. This relates especially to methods of assay.

That the author's efforts have been appreciated is indicated by the fact that the first edition appeared in the fall of 1907 and was reprinted before this second edition. E. J. HALL.

NEW PUBLICATIONS

By D. D. Berolzheimer, Librarian, Chemists' Club, New York.

Acetone; The Direct Production of— from Wood-waste. By J. Otto. Thesis, Technical High School, Dresden. (German.)

Alloys; The Binary Metal -. By K. Bornemann. $2.25. Wilhelm Knapp, Halle. (German.)

Analysis; Commercial Organic—; Vol. VI. By A. H. Allen. 4th Ed. 8vo. $5.00. P. Blakiston's Son & Co., Philadelphia.

Brass; Principles and Practice of Burnishing, Lacquering and Bronzing Ware. By W. N. Brown. 2d Ed. 8vo. $0.75. Scott, Greenwood & Co., London.

Carbon Monoxid; The Testing for and Determination of—. 8vo., 69 pp. Thesis, Munich. (German.)

Coals; Steaming Tests of—, and Related Investigations. By L. P. Breckenridge, Henry Kreisinger and Walter T. Ray. 8vo., 380 pp. U. S. Bureau of Mines, Bulletin 23.

Emery and the Emery Industry. (Translation.) By A. Haenig. Cr. 8vo., 104 pp. $1.50. Oil and Colour Trades Journal, London.

Engineering Valuation of Public Utilities and Factories. By Horatio A. Foster. 8vo., 350 pp. $3.00. D. Van Nostrand Co., New York.

Explosives; The Use of Permissible—. By J. J. Rutledge. 8vo., 34 pp. U. S. Bureau of Mines, Bulletin 10.

Food, The Pure— Laws of Germany, Including Methods of Analysis. By K. von Buchka. 2d Ed. 8vo., 294 pp. $1.25. Julius Springer, Berlin. (German.)

Hydrogen; The Production of— from Carbon Monoxid and Lime. By W. H. Engels. 8vo., 55 pp. Thesis, Karlsruhe. (German.)

Metal and Iron Casting with Special Reference to Alloys for Machine Construction. By H. Wachenfeld. 8vo., 104 pp. $1.25. Halle, 1912. (German.)

Mines; First Annual Report of the Director of the Bureau of—. By Joseph A. Holmes. 8vo., 57 pp. Bureau of Mines, Washington, D. C.

Refractory; Production of— Substances. By G. Benfey. 8vo., 144 pp. $1.00. Hanover, 1912. (German.)

Refrigerating; The Absorption— Machine. By G. T. Voorhees. Cr. 8vo. $2.25. Spon & Chamberlin, New York.

Refrigerating Machinery, its Principles and Management. By A. R. Leask. 5th Ed. Cr. 8vo., 310 pp. $1.25. Simpkin, London.

Sewage; Practical Sewerage and— Disposal. By H. C. H. Stenton. 12mo., 148 pp. $1.00. Rogers, London.

Sewage Sludge. By A. Elsner, *et al.* Roy. 8vo. $2.75. Hill Publishing Co., London.

Smoke. A Study of Town Air. By Julius B. Cohen and A. R. Ruston. 8vo., 86 pp. $1.25. Edwin Arnold, London.

Smokeless; The— Combustion of Coal in Boiler Furnaces. 8vo., 188 pp. U. S. Bureau of Mines, Bulletin 40.

Soap; Manual of Toilet— Making. (Translation.) By C. Deite. Demy 4vo. $3.75. Oil and Colour Trades Journal, London.

Steel; Sampling and the Analysis of Iron and—. By O. Bauer and E. Deiss. Lex. 8vo., 258 pp. $2.25. Julius Springer, Berlin. (German.)

Sugar; Methods for— Analysis and Allied Determinations. By Arthur Given. 8vo. $2.00. P. Blakiston's Son & Co., Philadelphia.

Tables; Hering's Ready Reference . By Carl Hering. New Ed. 16mo., 196 pp. $2.50. John Wiley & Sons, New York.

Textile; The German— Industry. By A. Oppel. L. 8vo., 167 pp. $1.50. Leipzig, 1912. (German.)

Water Analysis for Sanitary and Technical Purposes. By Herbert B. Stocks. 8vo., 102 pp. $1.25. Chas. Griffin & Co., London.

Smoke; The— Problem at Boiler Plants. By D. T. Randall. 8vo., 31 pp. U. S. Bureau of Mines, Bulletin 39.

Spectra; The— of the Elements at Normal Pressure. By F. Exner and E. Haschek. L. 8vo., 332 pp. $7.00. Vienna, 1912. (German.)

RECENT JOURNAL ARTICLES OF INTEREST TO THE INDUSTRIAL CHEMIST.

Ammonium Sulfate; The Binding of Ammonia alone or together with Hydrogen Sulfid by Sulfurous Acid with the Simultaneous Formation of— and Free Sulfur. By Walther Feld. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 15, pp. 705–711.

Cements; The Theories of the Hardening of the Hydraulic—, Based on the Latest Observations. By Ferdinand M. Meyle *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 15, pp. 711–718.

Corrosion; The Influence of Carbon on the— of Steel Anonymous. *Engineering Record*, Vol. 65, 1912, No. 1 pp. 426–427.

Iron; The Mineral Sulfides of—. By E. T. Allen, J. L. Crenshaw and John Johnson. *American Journal of Science* Vol. 33, 1912, No. 195, pp. 169–236.

Oils; Action of Sulfur Dioxid upon— and their Fatty Acids By S. A. Hird and L. L. Lloyd. *Journal of the Society of Chemical Industry*, Vol. 31, 1912, No. 7, pp. 317–319.

Oils; Methods for Testing Lubricating—. By T. D. Simpson *Journal of the American Leather Chemists' Association*, Vo 7, 1912, No. 5, pp. 235–243.

Paint; Recipes for the Colour, —, Varnish, Oil, Soap and Dry Saltery Trades. Anonymous. New Ed. Demy. 8vo. 330 pp. $3.00. *Oil and Colour Trades Journal*, London.

Pulp; The Technical Development of the Manufacture of Sulfite By Spiro. *Chemiker Zeitung*, Vol. 36, 1912, No. 53, 1 494–496.

Rare Earths; Bibliography of the—. By C. Richard Boehm *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 1 pp. 758–761.

Soap; Modern Development of the— and Crude Glycerin Industr By Franz Goldschmidt. *Zeitschrift fuer angewandte Chemi* Vol. 25, 1912, No. 17, pp. 808–816.

Sugar; Comparison of the Methods of Heating and Evaporatic Developed in Beet and Cane— Factories. Anonymou *International Sugar Journal*, Vol. 14, 1912, No. 160, 1 199–210.

Tar; The Determination of— in Generator Gas. By A. Gwig ner. *Chemiker Zeitung*, Vol. 36, 1912, No. 50, pp. 461–4

Turpentine; The Determination of Benzine and Benzol Hydr carbons in . By J. Marcusson. *Chemiker Zeitung*, V 36, 1912, Nos. 45 and 46, pp. 413–414 and 421–422.

RECENT INVENTIONS

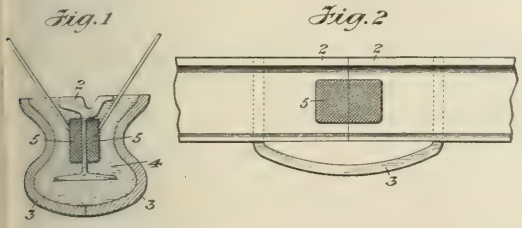
Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

PROCESS OF WELDING METALS.

U. S. Patent No. 1,021,318, to Anton Mucas, of New York, N. Y. Assignor to Goldschmidt Thermit Company, of New York, N. Y.

This is a process of uniting two metals (one of which is solid) by the action of cast metal.

The feature which distinguishes the process from other processes of uniting metals by the action of molten cast metal upon one or more solid pieces of metal is the employment in conjunction with ordinary molten metal of thermit and the superheated molten metal resulting from the thermit reaction for



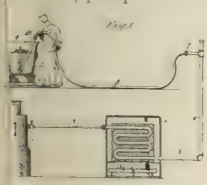
raising the temperature of such molten cast metal sufficiently to cause the melting of the solid metal or metals acted upon and the consequent union of all three kinds of metal into a substantially homogeneous body metal.

The illustration shows the application of the process to the welding of the railroad rails, the ends of the rails to be joined being placed in a mold, 3, and the thermit mixture 5, consisting of oxid of iron and finely divided aluminum, being held in position on each side of the joint by rods.

TREATMENT ON METALS.

S. Patent No. 1,019,965, to William H. Kelly, of Los Angeles, California.

This is a process of effecting the purification of molten metals from sulfur, phosphorus and other like impurities by subjecting them to the action of partly dissociated steam, such steam containing nascent hydrogen and nascent oxygen.

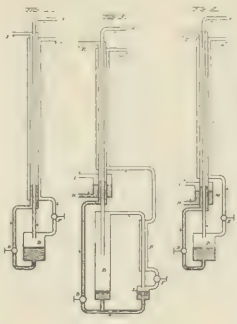


The steam is produced in the boiler 1, shown in the accompanying illustration, and partly dissociated in the retort 2 from which it is conducted to the nozzle 9 immersed in the molten metal.

PROCESS FOR THE PRODUCTION OF HYDROGEN FROM GAS MIXTURES CONTAINING HYDROGEN.

U. S. Patent No. 1,020,102, to Carl von Linde, of Münich, Germany.

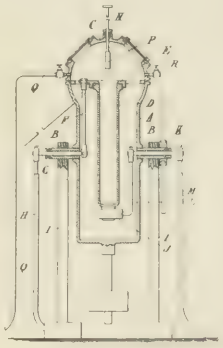
In the use of the apparatus illustrated the compression gas mixture enters at A after it has been previously freed from such constituents or impurities which can bring about stoppages in the liquefying apparatus, *e. g.*, carbonic acid and sulfur compounds. In its passage through the apparatus to the vessel B, the gas mixture reduced in temperature to such a degree in the temperature-interchanger C, that the greater part of the constituents of the gas mixture are liquefied and collected in the vessel B. The liquefied portion flows out of this vessel through the expansion mechanism D into the interchanger C, evaporates and thereby removes heat from the compressed gas mixture flowing through the apparatus. The products of this evaporation, *e. g.*, carbon monoxid, escape at E, after an interchange of temperature with that of the compressed gas mixture passing through the apparatus and can be applied in any manner desired. The portion of the gas mixture which is not liquid (hydrogen and the remaining constituents) after passing through the expansion mechanism F flows through the temperature interchanger C in an opposite direction to that of the compressed gas mixture and escapes out of the apparatus at G at normal temperature.



APPARATUS FOR MELTING AND MIXING METALS IN VACUUMS.

U. S. Patent No. 1,015,091, to Wm. Speirs Simpson, of London, England.

This invention relates to apparatus for melting and mixing metals *in vacuo* of the kind in which electrical heat is used for melting the metals, and the object is to construct an improved apparatus for removing volatilizable impurities from certain easily oxidizable metals, such as aluminium, magnesium, calcium and the like with which it is desirable for forming useful alloys; the hitherto unavoidable oxidation of these metals while in a molten state is prevented and effective mixing and alloying under the most favorable conditions is accomplished; the result affords a purified metal or alloy of uniformly superior quality and strength.



The invention is carried out in a receptacle or chamber of suitable size and dimensions wherein a comparatively high vacuum may be created and maintained by means of a vacuum pump in any convenient manner. Inside the chamber is placed a crucible made of refractory or carbonaceous material for containing the metals to be treated: these are heated by means of an electric current applied to the top and bottom of the crucible.

The apparatus consists of a vacuum chamber with a body portion having trunnions for mounting it tiltably; a cover removably applied to its upper end and adapted to form a fluid-tight connection; a crucible contained within and carried by the body portion; an interior chamber to contain a charge to be treated and having its mouth arranged toward the top of the body portion; means for conducting a heating medium to the crucible through the trunnious of the tiltably mounted body portion.

MARKET REPORT.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF MAY.

ORGANIC CHEMICALS.

Acetanilid	Lb.	20 1/2	@	23
Acetone (drums)	Lb.	17	@	18
Alcohol, grain (188 proof)	Gal.	2.56	@	2.58
Alcohol, wood (95 per cent.)	Gal.	50	@	52
Alcohol, denatured (180 proof	Gal.	40	@	42
Amyl Acetate	Gal.	2.90	@	3.00
Acetic Acid (28 per cent.)	C.	2.00	@	2.15
Aniline Oil	Lb.	10 3/4	@	11 1/2
Benzoic Acid	Lb.	23 1/4	@	28
Carbon Tetrachloride (drums)	Lb.	10	@	15
Carbon Bisulphide	Lb.	nominal		
Chloroform	Lb.	20	@	30
Carbolic Acid (drums)	Lb.	16	@	18
Citric Acid (domestic), crystals	Lb.	38 1/2	@	39
Camphor (refined in bulk)	Lb.	44	@	—
Dextrine (imported potato)	Lb.	6	@	7
Dextrine (corn)	C.	3.30	@	3.66
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8 1/2	@	9 1/2
Glycerine (dynamite)	Lb.	19	@	21
Oxalic Acid	Lb.	8 1/2	@	8 1/2
Pyrogallic Acid (bulk)	Lb.	1.35	@	1.45
Salicylic Acid	Lb.	32	@	34
Starch (corn)	C.	2.55	@	2.85
Starch (potato)	Lb.	5 1/4	@	5 3/4
Tannic Acid (commercial)	Lb.	35	@	35 1/2
Tartaric Acid, crystals	Lb.	30 1/2	@	31

INORGANIC CHEMICALS.

Acetate of Lime (gray)	C.	2.50	@	2.60
Acetate of Lead (brown, broken)	Lb	7 3/4	@	8
Alum (lump)	C.	1.75	@	2.00
Ammonium Carbonate, domestic	Lb.	8	@	8 1/4
Ammonium Chloride, gray	Lb.	6 1/8	@	6 1/4
Aluminum Sulphate	C.	90	@	1.75
Aqua Ammonia (drums) 16°	Lb.	2 1/4	@	2 1/2
Arsenic, white	Lb.	4	@	4 1/8
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Barium Chloride	C.	1.40	@	1.55
Barium Nitrate	Lb.	4 3/4	@	5
Borax, crystals (bags)	Lb.	3 1/2	@	4
Boric Acid, crystals (powd.)	Lb.	7	@	7 1/2
Bromine, bulk	Lb.	25	@	30
Bleaching Powder (35 per cent.)	C.	1.22 1/2	@	1.30
Barytes (prime white, foreign)	Ton	18.50	@	22.50
Blue Vitriol	Lb.	5 1/2	@	5 3/4
Calcium Chloride	C.	65	@	90
Chalk (light precipitated)	Lb.	4 1/2	@	6
China Clay (imported)	Ton	11.50	@	18.00
Feldspar	Ton	7.00	@	9.00
Fuller's Earth, powdered	C.	80	@	85
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1.15	@	1.55
Iodine (resublimed)	Lb.	2.60	@	2.65
Lead Nitrate	Lb.	8 3/8	@	8 1/2
Lithium Carbonate	Lb.	65	@	70
Magnesite (raw)	Ton	7.50	@	8.50
Nitric Acid, 36°	Lb.	3 7/8	@	4 1/4
Phosphorus	Lb.	35	@	90
Phosphoric Acid, sp. gr. 1.75	Lb.	22	@	26
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bromide	Lb.	31	@	34
Potassium Permanganate (bulk)	Lb.	9 3/4	@	10
Potassium Cyanide (bulk) 98–99 per cent.	Lb.	19 1/2	@	21
Potassium Iodide (bulk)	Lb.	2.10	@	2.15
Potassium Chlorate, crystals	Lb.	8 1/4	@	9 1/2
Potassium Nitrate (crude)	Lb.	4 1/2	@	4 3/4
Potassium Bichromate, 50°	Lb.	6 7/8	@	7
Quicksilver	Flask	41.00	@	43.00
Salt Cake (glass-makers')	C.	55	@	65
Silver Nitrate	Oz.	39	@	40
Soapstone in bags	Ton	10.00	@	12.00
Sodium Acetate	Lb.	4 1/4	@	5
Sodium Chlorate	Lb.	8 1/4	@	9 1/2
Sodium Bicarbonate (English)	Lb.	2 3/4	@	3
Sodium Bichromate	Lb.	5	@	5 1/4
Sodium Hydroxide, 60 per cent.	C.	1.70	@	1.75
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent., spot	C.	—	@	2.45
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	6 7/8	@	7 3/8
Sulphur, Roll	C.	1.85	@	2.15
Sulphur, Flowers (sublimed)	C.	2.20	@	2.60
Sulphuric Acid, 60° B.	C.	85	@	1.00
Talc (American)	Ton	15.00	@	20.00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	13 1/4	@	13 1/2
Tin Oxide	Lb.	47	@	51
Zinc Chloride (granulated)	Lb.	4 1/4	@	4 1/2
Zinc Sulphate	Lb.	2 1/4	@	2 1/2

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	36	@	40
Black Mineral Oil, 29 gravity	Gal.	12	@	12 1/2
Castor Oil (No. 3)	Lb.	9 1/2	@	10 1/2
Ceresin (yellow)	Lb.	9	@	15
Corn Oil	C.	6.15	@	6 1/4
Cottonseed Oil (crude), f. o. b. mill	Gal.	46	@	48
Cylinder Oil (light, filtered)	Gal.	19 1/2	@	20
Japan Wax	Lb.	9 1/2	@	10
Lard Oil (prime winter)	Gal.	85	@	90
Linseed Oil (double-boiled)	Gal.	75	@	78
Paraffine Oil (high viscosity)	Gal.	25 1/2	@	26
Paraffine (crude 120 & 122 m. p.)	Lb.	3	@	3 3/8
Rosin Oil (first run)	Gal.	38	@	40
Spindle Oil, No. 1	Gal.	16	@	16 1/2
Sperm Oil (bleached winter) 38°	Gal.	74	@	76
Stearic Acid (double-pressed)	Lb.	9	@	10
Tallow (acidless)	Gal.	60	@	63
Tar Oil (distilled)	Gal.	30	@	31

METALS.

Aluminum (No. 1 ingots)	Lb.	20	@	20 1/2
Antimony (Hallet's)	Lb.	7 3/4	@	8
Bismuth (New York)	Lb.	2.10	@	2.15
Copper (electrolytic)	Lb.	16 1/4	@	16 3/8
Copper (lake)	Lb.	16 3/8	@	16 1/2
Lead, N. Y	Lb.	4.20	@	—
Nickel	Lb.	40	@	45
Platinum (refined)	Oz.	45.50	@	46.00
Silver	Oz.	61 3/8	@	—
Tin	Lb.	46 1/2	@	46 3/4
Zinc	Lb.	6.85	@	—

FERTILIZER MATERIALS.

Ammonium Sulphate	C.	3.40	@	3.45
Fish Scrap, domestic, dried	Unit	2.75	@	10
Blood, dried	Unit	2.75	@	2.80
Tankage, high grade	Unit	2.65	@	10
Bone, 4 1/2 & 50, ground, raw	Ton	27.00	@	—
Potassium, "muriate," basis 80 per cent.	Ton	38.55	@	—
Phosphate, acid, 16 per cent	Ton	7.25	@	7.50
Phosphate rock; f. o. b. mine:				
Florida land pebble 68 per cent.	Ton	3.70	@	3.80
Tennessee, 68–72 per cent.	Ton	4.25	@	4.50
Pyrites, furnace size, imported	Unit	0.13 1/2	@	—
Castor meal	Unit	2.75	@	—
Mowrah meal	Ton	8.50	@	9.00

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume IV JULY, 1912 No. 7

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Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered at the Post-Office, Easton, Pa., as Second-class Matter.

ESCHENBACH PRINTING COMPANY, EASTON, PENNA.

TABLE OF CONTENTS

EDITORIALS:
- The Production of Ethyl Alcohol from Waste Products 478
- Occupational Diseases 480

ORIGINAL PAPERS:
- Corrosion of Iron in Pure Water and Air Combined; the Electrolytic Theory Again Confirmed. By William R. Fleming 480
- The Relative Corrosion of Iron and Steel Pipe as Found in Service. By William H. Walker 486
- Description of the Explosion Test at the Experimental Mine of the United States Bureau of Mines, February 24, 1912. By George S. Rice 488
- The Expansion Coefficient of Graphite. By Arthur L. Day and Robert B. Sosman 490
- A Volumetric Method for the Determination of Thorium in the Presence of Other Rare Earths. The Analysis of Monazite Sand. By F. J. Metzger and F. W. Zons 493
- The Resenes of Resins and Oleoresins. By Chas. H. Herty and W. S. Dickson 495
- A Method of Examining China Wood Oil. By Parker C. McIlhiney 496
- On the Indices of Refraction of China Wood Oil. By Louis Elsberg Wise 497
- The Refractive Index of Beeswax. By L. Feldstein 498
- The Chemistry of Anaesthetics, IV: Chloroform. By Charles Baskerville and W. A. Hamor 499
- Laboratory Studies of Rennin. By A. Zimmermann 506
- Micro-Chemical Tests for the Identification of Some of the Alkaloids. By Earl B. Putt 508
- An Improved Method of Assay for Aromatic Sulfuric Acid. By Linwood A. Brown 512
- A Method for Assaying Spirits of Camphor. By Arthur T. Collins 514
- Suggested Modifications to the U. S. P. Assay of Opium. By R. Norris Shreve 514
- A Note on the Determination of the Digestive Value of Papain. By J. R. Rippetoe 517
- The Bromine and Iodometric Methods for the Volumetric Determination of Cresol. By C. M. Pence 518
- The Accurate Volumetric Determination of Phosphoric Acid in Phosphate Rock. By John G. Fairchild 520
- The Determination of Total Manganese in Soils. By Ross A. Gortner and Clayton O. Rost 522
- Altering the Composition of Indian Corn by Seed Selection. By L. H. Smith 524
- Relation of Active Potash to Pot Experiments. By G. S. Fraps 525
- The Detection of Formic Acid in Fruit Products. By F. L. Shannon 526
- The Detection of Prussian Blue in Tea. By Fred West 528

LABORATORY AND PLANT:
- Factors Determining the Capacity of a Filter Press. By C. Almy, Jr., and W. K. Lewis 528
- Improved Sulphuric Acid Chambers. By Thomas H. Norton 532
- A Modification of the Frary Electrodynamic Stirring Device. By J. M. Knbte and W. R. Work 534
- The Underwriters' Laboratories Extraction Apparatus. By Henry J. Cary-Curr 535

ADDRESSES:
- The Present Status of the Gas Industry and its Outlook. By Charles E. Munroe 536

CURRENT INDUSTRIAL NEWS:
- Selenium Glass 539
- Heavy Oil Engines 540
- The Classification of Soaps 541
- The Spontaneous Combustion of Charcoal 541
- Artificial Rubber from Seaweed 542
- "Tempered Copper" Tools 542
- The Purification of Air by Ozone 542
- The Use of Coke-Oven Gas 542
- The Preservation of Wood with "Bellit" 542
- Chrome-Nickel Bronze 542

NOTES AND CORRESPONDENCE:
- Notes on the Composition and Analysis of Desiccated Milk and Cream 543
- A Modification of the Babcock Test as Applied to the Estimation of Fat in Desiccated Milk 544
- Alundum not Constant in Weight 544
- The Centenary of the Introduction of Gas 545
- American Electrochemical Society Research Fund 546
- Maine Section of the American Chemical Society 546
- Organization of Committees for Study of Industrial Diseases 547
- Organization of Rubber Section 547
- Paint and Varnish in the U. S. Navy 547
- A Colorimetric Method for the Determination of Carbon in Iron and Steel. A Note of Protest 547
- A Colorimetric Method for the Determination of Carbon in Iron and Steel—A Note 548
- Valuation of Fluorspar—A Correction 548
- General Bakelite Company Starts Infringement Suits 548
- The End of the Coöperative Glass Factories in Italy 548
- International Congress of Applied Chemistry. Announcement of Section I, Analytical Chemistry 548

BOOK REVIEWS:
- Corrosion of Iron and Steel; Technologic Papers of the Bureau of Standards, No. 3: Tests of the Absorptive and Permeable Properties of Portland Cement Mortars and Concretes, together with Tests of Dampproofing and Waterproofing Compounds and Materials; A Dictionary of Applied Chemistry; Allen's Commercial Organic Analysis; The Chemistry of Breadmaking; The Laboratory Apparatus Blue Book 549

NEW PUBLICATIONS 551

RECENT INVENTIONS 552

MARKET REPORT 554

EDITORIALS

THE PRODUCTION OF ETHYL ALCOHOL FROM WASTE PRODUCTS.

The first synthesis of ethyl alcohol was made about 1826, by Hennel, utilizing the reaction of ethylene and sulphuric acid to form sulphovinic acid which, upon heating with an additional quantity of sulphuric acid, yields alcohol. Berthelot improved this process by synthesizing ethylene from its elements *via* acetylene, and by making a more complete conversion of ethylene into sulphovinic acid.

The one source of the alcohol is the action of the zymase of yeast upon glucose and other fermentable sugars. The sources of the fermentable sugars may by grouped into two classes:

(1) The products of the hydrolysis of starch and allied substances by means of an amylase.

(2) Solutions of sugars obtained directly from fruits and plants and from the non-crystallizable by-products of sugar-works—such as molasses.

The most economical source of starch in our country is probably Indian corn costing about $21.00 per ton. One ton of corn gives about ninety gallons of 94 per cent. alcohol. About two gallons of raw molasses produce one gallon of 94 per cent. alcohol, and this raw material costs about $0.21 per gallon of 94 per cent. alcohol. The costs of the distillation of the mashes and the rectification and purification of alcohol cannot be entered into here, but the approximate cost of 95 per cent. alcohol (190 proof) to the consumer may be taken as about $0.50 per gallon, exclusive of taxation.

Within the last two or three years, two new commercial processes for the production of alcohol have been put in operation on a comparatively large scale. The purpose of this article is to present and discuss briefly from a chemical engineering standpoint these two processes: namely, the production of alcohol from sulphite cellulose waste lyes, and the production of alcohol from sawdust.

I. ALCOHOL FROM SULPHITE LYES.

In the sulphite process for the production of pulp, for every ton of cellulose there are about ten tons of sulphite lyes (T. H. Norton, *U. S. Cons. Rep.*, Nov., 1911) which contain one-half the weight of the wood originally introduced into the boilers. Among the substances present are: dextrose and other sugars, xylose, acetic acid, tannic acid, nitrogen compounds, methyl alcohol, resins, etc., and calcium lignin-sulfonate, the chief product of the reaction. Most of the sugars in these lyes are fermentable and they constitute about 1 per cent. of the lyes, the yield of alcohol being from fifteen to seventeen and one-half gallons per ton of cellulose [C. G. Schwalbe, *Z. angew. Chem.*, **23**, 1537(1910)].

Recently in Sweden two industrial processes have been developed, that of Ekström (P. G. Ekström, Eng. Pat. 6741, March 17, 1910) at Skutskär and that of Wallin at Forss. These processes are practically identical, differing only in the neutralization of the acid. The former uses lime, chalk, etc., and the latter waste causticization sludge. The general scheme is as follows: The lyes are first neutralized in large vats, then cooled in towers and aerated. In a mill producing ten tons of cellulose per twenty-four hours the volume of the lyes to be treated is about nine thousand gallons per day. A yeast nutrient, malt extract or dead yeast is added to the cool, neutral liquid which is transferred to the fermentation vats. After fermentation (which takes three days or more) the yeast is separated and the liquid distilled in a continuous still. The percentage of alcohol is very low and considerably more steam is used in the distillation than is required with mash from molasses which usually contains about 7 per cent. alcohol by volume. The alcohol obtained is already denatured as it contains considerable methyl alcohol (from the unfermented lyes), furfurol, aldehydes, and sometimes acetone, but is practically free from terpenes.

The above process with a few minor changes is being worked on a large scale at several places in Sweden. The experimental plant at Skutskär began operations on May 24, 1909, using waste lyes from a 5,000-ton cellulose plant. In March, 1910, 560 gallons of "normal strength" alcohol were produced per 24 hours. The total for the month was about 13,000 gallons. The process yields about 6 gallons of absolute alcohol for 1000 gallons lye, and about 14 gallons for every ton of cellulose.

As the alcohol produced from waste lyes is denatured, its chief uses will necessarily be for heating and other industrial purposes. The industrial prospects of this process depend on the cost of production, conditions of taxation and capacity of the market. Estimates of the cost of production for a mill producing 340,000 gallons per annum place the cost at about $9.50 per 100 gallons. In Sweden the tax per gallon increases with the output, so that for an annual production of 340,000 gallons, the cost of production including the tax is about $15.50 per 100 gallons. In Germany excise regulations penalize new distilleries so that in addition to the cost of production, sulphite spirit would be subject to a tax of about $17.00 per 100 gallons. Regarding the capacity of the market, in Sweden during the fiscal year 1908–1909 the total production of alcohol was about 5,800,000 gallons (absolute) and the imports were about 310,000 gallons. The sulphite lye mill at Larkudden is reported as having produced spirit during the year 1910 at the rate of 157,000 gallons per annum, and the annual rate of production at the present time is estimated at 250,000–400,000 gallons. The pulp mills of Sweden can produce 6,500,000 gallons of absolute alcohol per annum. It must be remembered that the present method of production from grain is always intimately connected with the agricultural industries of the country, and therefore will not be easily displaced. Also, while under special conditions (especially low taxation) the

sulphite process can be worked at a profit, yet it does not solve the problem of the disposal of the waste lyes, as only about 1 per cent. of the total weight of lyes is converted into alcohol. In fact on account of the presence of dead yeast, etc., the problem of the disposal of the lyes may be aggravated by the use of this process.

II. ALCOHOL FROM SAWDUST.

The cost of raw material is always of great importance in any industry. While Indian corn costs about $21.00 per ton, sawdust in the vicinity of a large mill where it is a by-product can be bought at a cost of 30–50 cents a ton including handling and transportation (short distances). One ton of sawdust calculated to the dry basis can yield 20 gallons of 94 per cent. alcohol, which makes the cost of this raw material 2–2½ cents per gallon 94 per cent. alcohol, as against 24 cents for Indian corn.

For nearly one hundred years it has been known to chemists that fermentable sugars can be produced from sawdust. The reaction is usually spoken of as being very simple, all that is necessary being to add a molecule of water to the cellulose. This hydrolysis is probably as complex as it is baffling. The unknown composition of those polysaccharides which we call cellulose and the very different results obtained on hydrolysis under slightly different conditions of catalyzer, temperature and pressure indicate that somewhat intricate reactions occur, the complete chemistry of which is not known at the present time. A very large number of patents have been granted on this reaction, the main differences being in method of manipulation and the catalyzing acid used. Sulphuric acid has been used in many cases but the subsequent removal of this acid has proved a serious stumbling-block. No process that was capable of commercial application had been devised until the year 1900 when Dr. Alexander Classen was granted his first patent. The more important English patents granted him are: No. 258, Jan. 4, 1900; No. 4,199, Feb. 27, 1901; No. 12,588, June 20, 1901. "Process claimed consists in boiling cellulose in a closed vessel at a temperature of 120–145° C. with a solution containing sulphurous and sulphuric acids or sulphurous and hydrochloric acids. A solution of 2 per cent. or more of sulphurous acid and 0.2 per cent. sulphuric acid is mentioned. The sulphuric acid may be conveniently formed in the boiler by admission of air or other suitable oxidizing agent. In this way concentrations of 10 per cent. sugar may be obtained, 80–90 per cent. of which is fermentable. Conversion is complete in 15 minutes."

An experimental plant using this process was erected at Aachen and a similar plant on a larger scale was built at Highland Park near Chicago. The results were satisfactory so that it was decided to build a commercial scale plant at Hattiesburg, Miss. The capacity of the conversion cylinder was two tons. After the conversion the acid was neutralized, cleared by subsidence, pumped into large vats and fermented by yeast and then distilled. From a commercial viewpoint this plant was a complete failure. From a chemical engineering standpoint it is an excellent example of a process which fell just short of success. The reasons given for the failure are: (1) Length of time required for conversion: 1½–2 tons requiring 4–6 hours. (2) Prolonged action produces gums and caramels and makes extraction of the sugar tedious and expensive. (3) Large quantity of acid required. (4) Lining difficulties, especially with lead linings.

Two chemical engineers, Ewen and Tomlinson, studied and undertook to improve this process. Their patent U. S. 938,308, 1909 describes their process. The converter used by Classen was about thirty feet in length and had a diameter of three feet, whereas in the Ewen and Tomlinson process the digester is much shorter, usually being about twelve feet in length and eight feet in diameter. The latter line their converter with fire-brick instead of using the troublesome lead lining. The operation seems to be fairly simple. Sulphur dioxide gas to the extent of 1 per cent. of the weight of the wood is introduced into the cylinder and live steam is turned on until a pressure of 100 lbs. is obtained. The steam is then turned off and the cylinder slowly revolved for 40–45 minutes, the temperature and pressure being kept constant. The total time of conversion is about one hour as against 4–6 hours in the old process. In operating this process it is important to raise the temperature as quickly as possible to the "critical point" which is defined as "that temperature above which the production of unfermentable substances and the destruction of the sugars become excessive and lies between 135° and 163° C." After extraction, the converted lyes have a total acidity of 0.64 per cent. (calculated to H_2SO_4) containing sulphuric, acetic acids, a small amount of sulphurous acid and aromatic compounds of the type of pyrogallol. These liquors contain about 5½ per cent. of reducible sugars calculated to dextrose. Polyphenols, tannin and furfurol are usually present in small amounts. These liquors are fermented and distilled in the usual manner, some care being required in the fermentation to have present a proper food for the yeast. The distilled alcohol obtained is potable, free from the odor and taste of wood, and from methyl alcohol and fusel oils, but contains traces of furfurol and aldehydes. One and one-half tons of dry wood give about 61½ gallons of 94 per cent. alcohol. From figures obtainable it appears that the efficiency of the process is from 75–80 per cent. of the theoretical yield of alcohol.

The Dupont Powder Company is operating a plant at Georgetown, South Carolina for the production of alcohol from waste woods. This plant is licensed under the Ewen and Tomlinson patents, and while no figures were obtainable, it is stated that experiments so far indicate the ultimate success of the process.

W. P. Cohoe is the inventor of a process for making fermentable glucose-like substances from cellulose and ligneous materials (U. S. Patents 985,725, 985,726, 1911). The conversion is done in two stages: first, steam is used producing acetic acid which is collected, and then steam and HCl vapors are introduced into the converter. The raw material used is generally sawdust.

The cost of production of alcohol by the sawdust process (Ruttan, *J. Soc. Chem. Ind.*, **1909**, p. 1290) is said to be about equal to that of grain, although there is such an enormous difference between the cost of the raw materials. One company, however, claims to be able to manufacture alcohol by the sawdust process at a cost of $0.07 per gallon.

Without going into the details of the chemistry involved, it is striking that, although the patents claim a conversion of cellulose into sugar, the so-called true fibrous cellulose, absorbent cotton, does not yield to this treatment. Also the material left after treatment contains cellulose which upon re-treatment yields but traces of fermentable sugar. Although authorities differ, it is claimed by some that the acid acts as a catalyzer hydrolyzing the lignone complex and a proportion of the "easily attacked cellulose." The oxycellulose and the "true cellulose" are said not to be seriously altered chemically.

It would seem that there is a possibility that a process might be evolved where the alcohol conversion of the wood pulp might be made first, and then the residue subsequently utilized for the production of paper pulp.

ALCAN HIRSCH.

OCCUPATIONAL DISEASES.

This subject is now receiving the attention it deserves. Hitherto the matter of diseases peculiar to industries has been in the hands of physicians. While medical men are competent to treat and cure such diseases it can readily be seen that they are unable by nature of their training to accomplish much in the elimination of the causes of occupational diseases. The physician is not the proper person to suggest to a manufacturer such changes in his processes as will eliminate the causes of the peculiar occupational ills to which his employees are subject. This is necessarily the function of the chemical engineer and it is to him that the physician now turns for assistance.

The June number of THIS JOURNAL published an address delivered by Dr. W. Gilman Thompson, Professor of Medicine in the Cornell University Medical College, in New York City, before the New York Section of the American Chemical Society. The attention of our readers is called to the facts set forth and the points brought out in this address, and chemists will readily see the opportunity which presents itself to them, to be of assistance in this crusade of the Twentieth Century.

The New York Section of the American Chemical Society has appointed a Committee on Occupational Diseases, which is now coöperating with a similar Committee of the New York Association for Labor Legislation. The personnel of these committees is given in another column of this issue. A joint meeting of the two committees was held on May 31st, at the Chemists' Club in New York City. This meeting was addressed by Dr. Alice Hamilton, whose work of investigating lead poisoning for the U. S. Department of Labor is well known. Dr. Hamilton spoke of the difficulties she had experienced in obtaining information, and laid particular stress on the importance of the coöperation of the chemist and physician.

It will be readily seen that this is a matter for organized and systematic work by our profession, and that the campaign must be one of educating the public, the workingman, and the manufacturer. It is evident that statistics must be collected so proper lines of work can be designed. More will be accomplished by education than by inconsidered or hasty legislation, and by this method the least possible hardship will be inflicted on established industries.

E. C. UHLIG.

ORIGINAL PAPERS

CORROSION OF IRON IN PURE WATER AND AIR COMBINED; THE ELECTROLYTIC THEORY AGAIN CONFIRMED.[1]

By WILLIAM R. FLEMING.

In a recent article in the *Iron and Steel Institute*,[2] Dr. J. Newton Friend again attacks the "Electrolytic" Theory of Corrosion. In his paper, a Carnegie Scholarship Memoir, he describes an experiment which demonstrates that "Pure water and pure air combined are without visible action upon pure iron." "This shows, Friend continues, that the electrolytic theory of corrosion is untenable, and definitely confirms the older acid theory."

In this paper I shall attempt to show that iron and steel *will* rust in pure water and air combined, if it is given a chance. Furthermore, I shall attempt to prove that Friend's experiment is a strong confirmation of the electrolytic theory, and not destructive to it.

We have to-day only two important theories of corrosion, the "Acid" and the "Electrolytic" theories.

[1] Read before the Cincinnati Section of the A. C. S., February 14, 1912.

[2] *Iron and Steel Institute*, **3**, 1 (1911).

The acid theory presumes that corrosion is primarily caused by acid attack. It denies the solubility of iron in pure water and denies that iron will rust in acid-free air and water combined.

The electrolytic theory presumes that iron is soluble in pure water, and that rust is subsequently formed through the influence of oxygen. The exposed surfaces of iron and steel contain segregated impurities which are supposed to give rise to differences of potential, in the presence of an electrolyte, which is generally moisture. At those points where the metal is anodic, iron passes into solution, assuming the ferrous ionic condition, while hydrogen is liberated at the cathode. Oxygen plays its part by depolarizing the hydrogen covered cathodes and by oxidizing the ferrous ions at the anodes. In its purest sense the electrolytic theory presumes that corrosion begins in a pure electrolyte, *e. g.*, water free from all traces of impurities.

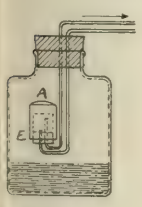
The defendants of the acid theory deny the solubility of iron in pure water and are emphatic in their claim that corrosion is "primarily the result of acid

attack." Since carbon dioxide is universally present in our atmosphere it is considered the chief cause of rusting. It attacks the iron forming ferrous carbonate and liberating hydrogen. Oxygen and moisture further react with the ferrous carbonate to form rust, freeing the carbon dioxide which in turn reacts with fresh iron. But, according to our latest notions of solutions, carbonic acid does not attack the iron directly, *e. g.*, in its atomic condition. It must first pass into solution (become ionic) before the acid can attack it. Therefore, the acid theory is but a special case under the general electrolytic theory. This has been admitted. But, while admitting the electrolytic character of corrosion, when viewed from the general standpoint of ionization as announced by Arrhenius, the defendants of the acid theory insist that iron will not assume the ionic state unless an acid is present in the electrolyte. Hence, they say, acid attack is the true beginning of corrosion.

There can be no doubt that the presence of acids (chiefly carbonic) has much to do with the *rapid* corrosion of our iron and steel. Without acids in our air and water the corrosion problem would be less formidable. This, however, is only a quantitative view-point. In attempting to get at the facts concerning the true cause of corrosion we should not allow ourselves to be blinded by mere quantitative ideas. Given pure iron in pure air and water, the factor of corrosion is very small. Likewise, with impure iron in impure air and water, the factor of corrosion is very great. But this does not interest us. We are concerned only with the true *starting point* of corrosion. It matters not how small the value of this "starting point," quantitatively, if iron is soluble in pure water even to the slightest extent, or, if iron will rust in pure water and air combined be it ever so slight, then this weakness in the metal itself is the true cause or starting point of corrosion. All influences which enter later are mere retarders or accelerators.

Below is given Friend's experiment and conclusions in his own words:

A-E is a hollow cylinder of iron or steel, closed at one end. The open end is plugged with a tightly fitting rubber stopper, bearing two glass tubes, arranged in such a manner that cold water can circulate through them. The glass bottle, containing about 100 cc. of twice normal caustic potash solution, is placed in a deep cold water bath, and heated gradually to 100° C. Its mouth is now closed with a large India-rubber bung, from which hangs the metal cylinder by the glass tubes—already alluded to—and the whole is thoroughly shaken to remove every trace of carbon dioxide from the walls, air, and surface of the iron. A current of cold water is now passed through the tubes, and on immersing the bottle again in the hot water bath, pure water vapor condenses upon A-E and drips off, rapidly washing it free from alkali. That the cylinder is actually free from alkali may be readily demonstrated by opening the apparatus, and testing with phenolphthalein, when no change in color occurs. Nevertheless, the iron remains perfectly bright for an indefinite number of days. An isolated spot of rust will often form here and there upon the surface of the metal, owing to the unavoidable traces of impurity always present in the purest metal obtainable, and if the apparatus is opened and the cylinder again polished with emery, the spots will appear again in the same places upon repetition of the experiment. Furthermore, where the iron is in contact with the India-rubber, a little corrosion takes place, owing to the presence of sulphur, etc. These points, however, do not affect the general result of the experiment. The conclusion is inevitable:



Dr. Friend's Apparatus.

"Pure water and pure air combined are without visible action upon pure iron."

This shows that the electrolytic theory of corrosion is untenable, and definitely confirms the older acid theory.

"The experiment was now repeated in every detail, save that the caustic potash was replaced by an equal amount of a saturated solution of barium hydroxide. Although in every other respect the experiments were precisely similar, the iron always rusted in the course of an hour or two. This shows that barium hydroxide is not sufficiently powerful to remove every trace of carbon dioxide from the air in the flask. In other words, its aqueous solution is in equilibrium with a definite, although minute, partial pressure of carbon dioxide. Now Moody employed aqueous barium hydroxide solution as his source of water distilled on to the iron in his apparatus. Consequently, his metal must have rusted had it not been protected by alkali dissolving out of the glass tubing containing it. A clear explanation is thus offered for the failure of Dunstan and of Walker, each working independently of the other, to confirm Moody's results, when a different kind of glass was employed in the construction of the apparatus—a glass which was slow to yield up any soluble alkali to liquid water condensed upon its surface."

No mention is made of conditions which might influence rusting of the metal. The temperature of the metal and water on its surface, and the rapidity with which this water is changed, are conditions which influence the results. These, along with other important conditions, will be taken up fully after describing my experiments. Suffice it to say here that my experiments prove that Friend is wrong in his conclusions, and that his experiment was concluded before he had proved anything.

The apparatus used in all experiments is shown in Fig. 1.

I and S are hollow metal blocks, $1 \times 1 \times 1^1/_2''$, with $^3/_4''$ hole $1^1/_4''$ deep. The samples in all cases received their final polishing on 0000 French emery paper.

The metal samples are connected by tubes for the circulation of cold water within them, as in Friend's experiment.

The purifying train consists of: A, dilute sulphuric acid; K_1, 50 per cent. potassium hydrate; K_2, 50 per cent. potassium hydrate; So, Soda lime; (the tube connecting bottle and train extends just to the bottom of the large rubber stopper); Sy, is a syphon; Cl, clamp on purifying train; C_2, clamp on syphon; C_3, large iron clamp for bolting down the rubber stopper.

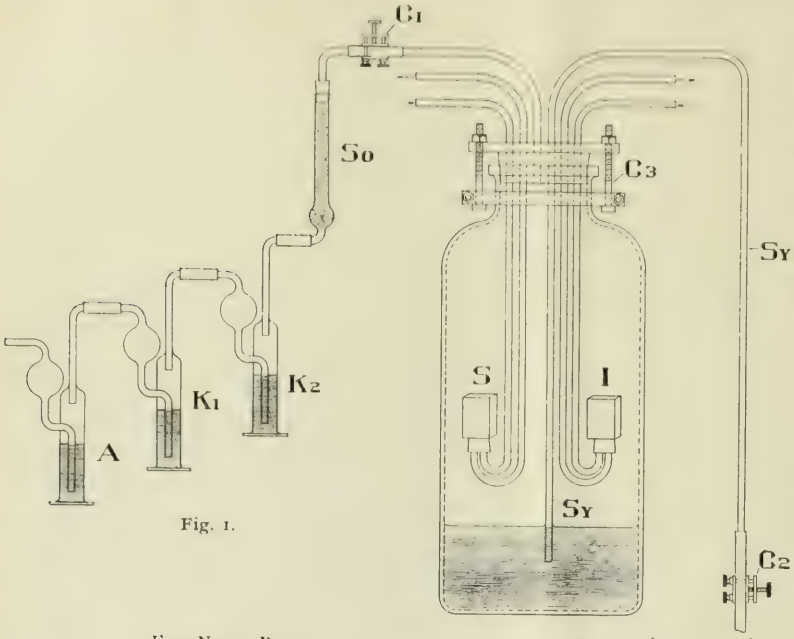


Fig. 1.

EXP. NO. 1, PART 1.

Metals Used. Genuine Open Hearth Iron and ordinary mild Open Hearth Steel.

	Analyses.					
	C.	Mn.	S.	P.	Si.	O.
Genuine Open Hearth Iron[1]	0.01	0.01	0.028	0.003	0.003	0.055
Open Hearth Steel	0.09	0.40	0.080	0.070	0.006	0.014

The bottle ($2\frac{1}{2}$ liters) was *completely* filled with saturated barium hydrate solution, recently boiled and filtered.

The large rubber stopper carrying the four condensing tubes, (with samples attached), syphon, and purifying train, was fitted tightly and bolted down securely by means of clamp C_3. No air bubbles were visible in the apparatus. The bottle was placed in a cold water bath and heat applied. C_2 was closed, and C_1 opened. The expanding solution filled the tube connecting the bottle and purifying train. Thus all air was expelled, and the necessity of removing carbon dioxide from the apparatus by mere shaking, avoided.

C_1 was then closed. C_2 was then opened to allow the expanding solution to fill the syphon. The solution was then syphoned off by opening C_1 just enough to allow the incoming air to bubble through the purifying train at the rate of four or five bubbles per second. When syphoned to the level indicated in Fig. 1, the clamp C_2, on syphon, was tightly closed. C_1 was left slightly open to avoid undue pressure or rarity of the air in the apparatus. The rubber stopper and all connections were well paraffined.

The water in the bath began to boil and cold water was made to circulate through the glass tubes and samples. Water immediately began dripping from the samples.

The experiment was continued thirty-five days. The water in the bath was boiling *every minute* during the whole period. Likewise, cold water was circulating rapidly through the condensing system. The temperature of the ingoing water was 4 to 5° C. The temperature of the water leaving the system varied from 10° to 15° C. At no time did it exceed 15°. From this the temperature of the metal samples was presumed to be about 8° to 12° C. The temperature of the pure condensed water vapor on their surfaces was probably but slightly higher. These conditions were maintained every minute during the thirty five days.

Observations:—At the end of thirty-five days not the slightest spot of rust or discoloration of any kind was visible on either the pure iron or the steel. Under the samples a ring of rust was formed by contact with the rubber stopper. This, of course, must be disregarded.

The surface area of the top and four sides of each sample was 7 sq. in. It is remarkable to think that 14 sq. in. of iron and steel can be exposed for thirty-five days to pure air and water combined without developing the slightest sign of a rust spot.

Conclusion:—This proves that iron or steel will not rust in pure air and water combined, provided the temperature of the metal does not exceed 15° C., and provided the temperature of the pure water condensing on its surface does not much exceed 15°; provided, also, that the pure water which condenses on their surfaces is being constantly renewed. Beyond this, the experiment *proves* nothing. It simply *indicates* that pure iron or steel will not rust in pure air and water combined.

EXP. NO. 1, PART 2.

At the end of thirty-five days the source of heat was removed and the apparatus taken out of the water bath. The circulation of the cold condensing water was continued until the barium hydrate solution had reached room temperature. The condensing system was then shut off. In a few hours the entire apparatus had reached room temperature, about 22° C. The metal samples were left covered with pure water, the flat tops completely, the sides with irregularly distributed patches or globules. This *same water* was destined to remain on the iron and steel until removed by natural evaporation at *room temperature*.

What was the effect of allowing the *same water* (at 22°) to remain on the metal (at 22°) for a protracted period? New conditions had been created in the apparatus.

Observations:—In fifteen hours the steel had developed thirty-three distinct rust spots and all of these spots were on areas covered with the pure water. The pure open hearth iron was still spotless. After twenty-four hours contact with the *same water* at 22° the steel contained about 50 spots; the iron was still rustless.

At the end of seventy-two hours the water had entirely evaporated from the sides of both metals. The tops were still covered with a thin layer of water. A few new spots had developed on the steel, but no rust had yet appeared on the iron.

At the end of eighty hours the water had evaporated

[1] Made by Newport Rolling Mill Co.

entirely from the tops. *Two large glaring spots of rust had developed on the top of the iron within the last eight hours.* More than seventy-two hours contact with the *same water* at 22° was necessary to produce rust on the pure open hearth iron. Less than fifteen hours contact with the *same water* produced rust on the steel.

Conclusions:—Iron or steel *will* rust in pure water and air combined if it is given a chance. The two most important factors which influence the development of rust are:

First, the temperature of the metal and of the pure water on its surface; second, the rate at which the pure water is renewed, changed, on the surface of the metal.

Exp. No. 2, Part 1.

The same samples were repolished and Exp. No. 1 repeated, except that the apparatus was kept in boiling water for six days instead of thirty-five.

Again, not the slightest sign of a rust spot developed on either sample.

Exp. No. 2, Part 2.

Apparatus cooled to room temperature as before. Rust developed in almost the same time on both the iron and steel, the iron requiring ninety hours contact with the same water, the steel about sixteen hours. The location of the rust spots does not seem to be determined entirely by impurities in the metal, but also by the distribution of the water patches on the surface.

This experiment confirmed Exp. No. 1 in every detail.

Exp. No. 3.

Same samples used. 2-*N* potassium hydrate substituted for barium hydroxide. Condensation period, six days.

This experiment confirmed Nos. 1 and 2, and further showed that either potassium hydrate or barium hydrate may be used with equal effect.

Exp. No. 4, Part 1.

Same samples used. Solution, saturated barium hydroxide. Condensation period, six days.

Both metals, as usual, were spotless at the end of six days.

Exp. No. 4, Part 2.

The flow of cold water through the condensing tubes was almost checked. The apparatus was kept in the boiling water bath. The slowly dropping water leaving the system showed a temperature of 55° C. From this I assumed that the temperature of the metal samples and of the pure water on their surfaces was about 55–60° C.

Under these conditions the condensation of water on the samples was almost stopped. Thus new conditions were created in the experiment. The metal samples were suspended in a hot atmosphere of air and water vapor, while the temperature of the metals themselves was about 55° C. and the temperature of the almost stagnant pure water on their surfaces was about 55° C.

Observations:—In one and one-quarter hours rust began developing on the top and sides of the steel. It developed so rapidly that it could be easily observed. Small clouds of insoluble matter came up from the metal and could be seen floating through the water. It had a faint greenish color. Presumably it was ferrous hydrate.

In two hours the pure iron began to develop rust. This, too, rusted so rapidly that it could be observed.

In a few hours the tops of the samples were covered with rust, and the sides were badly spotted.

Conclusion:—This experiment clearly demonstrates that pure open hearth iron and steel will rust, and rust badly, in pure water and air combined, provided the temperature of the metal and water on its surface is sufficiently high.

This, and all preceding experiments, further prove that rust develops much faster on steel (impure iron) than on pure open hearth iron. This is in strict accordance with the electrolytic theory.

Exp. No. 5, Part 1.

Samples, same. Solution, barium hydrate; condensation period, ten days.

No sign of rust at close of ten days.

Exp. No. 5, Part 2.

In Part 2, Exp. No. 4, the condensing water was only partially checked. In this experiment the condensing system was shut off entirely, the apparatus being kept in the boiling water. Accordingly, the temperature of the metals and pure water on their surfaces would be higher than in Exp. No. 4. From this increase in temperature should result an increased rate of corrosion. Such was the case.

In 25 minutes the top of the steel was badly rusted and the sides considerably spotted.

In 50 minutes the iron was badly rusted.

This further demonstrated the influence of temperature and of stagnant water.

Exp. No. 6, Part 1.

Different samples used.

	Analyses.					
	C.	M.	S.	P.	Si.	O.
Genuine Open Hearth Iron	0.01	0.040	0.026	0.004	0.003	0.056
Mild Open Hearth Steel	0.12	0.38	0.040	0.076	0.007	0.009

Solution, barium hydrate. Condensation period, twelve days. At the close of twelve days not the faintest suggestion of a rust spot was visible on either sample.

Exp. No. 6, Part 2.

After twelve days the source of heat was removed as in Exp. No. 1, Part 2.

The steel developed twenty-four rust spots in twenty hours. In ninety hours, over forty spots were visible.

The iron developed only three spots on top after ninety hours.

This rust development took place at room temperature (about 22°) while the same water remained on the metal until removed by natural evaporation.

Exp. No. 7.

Sample same as Exp. No. 6.

Solution, potassium hydrate.

Condensation period, six days.

No sign of rust, as usual.

Exp. No. 7, Part 2.

Exp. No. 5, Part 2, repeated to confirm results on different metals.

The steel began to develop rust in 35 minutes; the iron in one hour. In one and one-half hours both were badly rusted.

Exp. No. 8.

Other samples used.

	Analyses.					
	C.	M.	S.	P.	Si.	O.
Genuine Open Hearth Iron	0.01	0.03	0.027	0.003	0.003	0.061
Acid Open Hearth Steel	0.15	1.15	0.055	0.105	0.009	0.010

Solution, potassium hydrate.

Condensation period, ten days.

At the close of ten days not the slightest suggestion of rust

appeared on either sample. In this connection it is interesting to note the high percentage of impurities (especially the manganese) in the steel.

EXP. NO. 8, PART 2.

Cooled to room temperature as in Exp. No. 1, Part 2.

In eight hours the steel was covered with rust spots. The iron, as usual, required about ninety hours to develop a few rust spots.

Aside from confirming the results of preceding experiments, this experiment further indicates the influence of impurities on the rate of rust development. As we should expect, from the electrolytic theory, increased impurities greatly increase the rate of corrosion.

EXP. NO. 9, PART 1.

Sample, same as Exp. No. 8.

Solution, barium hydrate.

Condensation period, ten days.

No rust developed, as usual.

EXP. NO. 9, PART 2.

Condensing system entirely stopped, as in Exp. No. 5, Part 2.

In fifteen minutes the top of the steel developed rust.

In 25 minutes it was covered with rust. The sides were also badly spotted.

In 45 minutes the iron began to develop rust.

In one and one-half hours the top and sides were badly rusted.

EXP. NO. 10, PART 1.

Sample, same as Exp. No. 1.

Solution, 2-*N* potassium hydrate.

Condensation period, six days.

No sign of rust, as usual.

EXP. NO. 10, PART 2.

Exp. No. 1, Part 1, demonstrated that iron or steel will not rust, while the temperature of the metal and water on its surface does not exceed 15° C., and while the surface water is constantly changing. In this experiment the object is to determine whether iron or steel will rust while the metal and surface water remain below 10°, with the *same water* lodging on the metals.

This condition was created in the bottle by removing the apparatus from the boiling water, and continuing the flow of cold condensing water through the system. In a few hours the potassium hydrate solution had reached room temperature. The temperature of the incoming condensing water was 5°, the outgoing water 7°. Therefore the temperature of the metals and of the water on their surfaces was about 6°. This condition was maintained for thirty days. At the end of this period not the slightest indication of rust was visible.

This experiment further shows the great influence of temperature on the development of rust in pure water and pure air combined. It demonstrates that pure open hearth iron or ordinary mild steel will not rust in pure water and air combined, provided the temperature of the metal and water is constantly below 7° C. This has been demonstrated in Part 1 of each experiment, but this experiment further shows that the *same water* remaining on the metal has little effect if the temperature remains sufficiently low.

EXP. NO. 10, PART 3.

After thirty days the cold samples were still covered with water. The condensing system was stopped and heat applied to the water bath until the water had reached 60° C.

In two hours after the water had reached 60° the steel was spotted with rust.

In four hours the steel was badly rusted.

The pure open hearth iron was still spotless.

The temperature was increased to 80°. In thirty minutes the iron began to rust. One hour later the top was covered with rust and the sides badly spotted.

Starting from a low temperature (6°), as in this experiment, and gradually raising the temperature is an excellent means of determining the temperature necessary to produce rust. It also indirectly shows the solution pressure of the metals at different temperatures. And in this way I believe we can test in a most reliable way the ability of a metal to resist corrosion in service. There can be no doubt that metals of high solution pressure will rust much faster than metals of low pressure. By this experiment we can compare these pressures, indirectly.

The carrying out of the experiment, however, is not extremely simple. It requires great care and in the hands of a careless operator it might become misleading.

I must call attention to the way in which rust developed in these experiments at higher temperatures. At these temperatures rust developed so rapidly that observations could be made at different stages.

When rust began to develop, the metal, over a small area, assumed a light grayish color. This gradually gave way to green, which increased in intensity for a few minutes, then gradually changed to yellow or rust color.

These observations strongly indicate that rusting, in a pure electrolyte (water free from acids, bases, etc.) is due to causes which have been properly explained as follows:

Pure water is dissociated to a certain extent. It contains dissociated hydrogen and hydroxyl ions. For the present purpose let $\overline{H}$ represent the hydrogen ion, $\overline{OH}$ the hydroxyl ion, $\overline{Fe}$ the iron ion, etc., and H, OH and Fe represent the atomic state of the element. At the anodic points iron passes into solution,

$$Fe = \overline{Fe}, \text{ and}$$

at cathodic point hydrogen is liberated;

$$\overline{H} = H$$

Iron and hydroxyl ions then unite chemically, to form ferrous hydroxide;

$$\overline{Fe} + 2\overline{OH} = Fe(OH)_2$$

Ferrous hydroxide then reacts with water and dissolved oxygen,

$$2Fe(OH)_2 + O + H_2O = 2Fe(OH)_3,$$

which is immediately converted to the hydrated oxide,

$$2Fe(OH)_3 = Fe_2O_3(3H_2O).$$

Iron Dissolves in Pure Water and Oxygen.—If, according to the electrolytic theory, iron passes into solution in pure water, a highly polished surface should be "etched" in spots during corrosion and it should reveal the structure of the metal somewhat as by etching with dilute acids or other reagents. We know that iron passes into solution when in contact with acids. We know that structure is developed on highly polished surfaces because the metal dissolves more rapidly along the boundary lines of the grains. Therefore, if iron passes into solution in pure water the surface will be etched and structure developed. Pure water will thus act as an exceedingly dilute acid. Microscopic examination of both the pure iron and steel after each of my experiments invariably showed the true structure of the metal in many places. Most of the surface, of course, was covered with rust and

the structure obscured, but large spots of rust invariably showed the structure of the metal in many places.

Fig. 2 shows the surface of the iron before using in Exp. No. 10. Fig. 3 shows the ferrite structure which was developed in several places in the large spot of rust on top of the sample. The grains are large. A portion of the metal which was free from rust was later etched with dilute nitric acid and the same structure appeared. Fig. 4 shows the steel before Exp. No. 10; Fig. 5, the structure in places after corrosion. The ferrite grains are small and mingled with pearlite, which accounts for the structure not being as well defined as it is in the case of pure iron. The small dark areas are pearlite; some of them show lamellar structures under higher powers. It will be observed that the oooo emery scratches have been almost entirely eroded.

This proves conclusively that iron is soluble in pure water, free from all traces of acids and containing only dissolved air. It further confirms the electrolytic theory since the structure of the metal is developed only in spots—anodic points where iron passes into solution.

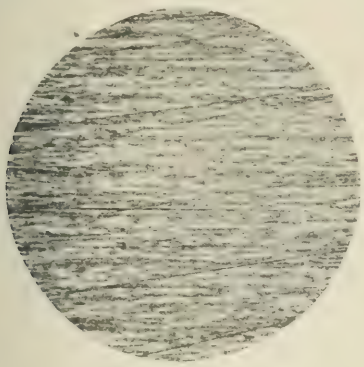


FIG 2 × 120.

Friend observed that spots of rust formed "here and there" on the surface of his metal but disregarded it as meaningless and as having no effect on the general conclusions. These spots, however, had great significance.

In every one of my experiments, Part 1, six different kinds of iron and steel were exposed from six to thirty-five days, and not the slightest spot of rust developed, not one minute spot on 42 sq. in. of metal. Compare this with Friend's "here and there" spots. Why did not a single spot develop in all my experiments? Simply because, in Part 1 of each, the temperature of the metals and pure water on their surfaces was kept below a certain fixed point (15° C). As the temperature of metal and water gradually increases a point is reached where "here and there" spots are developed. Was this due to impurities in the metal at these points? Yes, partially. But it was probably due mostly to the increase in solution pressure of the iron at these points, resulting from increased temperature. The surface of each metal contained points of lowest and points of highest solution pressure, and other points between these extremes. Now, with increasing temperature, the points of highest solution pressure developed rust first while the points of lowest pressure were slowest to rust. Along this line of reasoning, increasing temperature should result in an increased number of rust spots on the metal. My experiments bore this out completely. Friend gives us no information about conditions in his experiment, but, from my experiments I am convinced that his "here and there" spots were formed because the temperature was higher than in Part 1 of my experiments, or because his samples were so impure that the solution pressure at places caused rust to develop even at low temperatures.

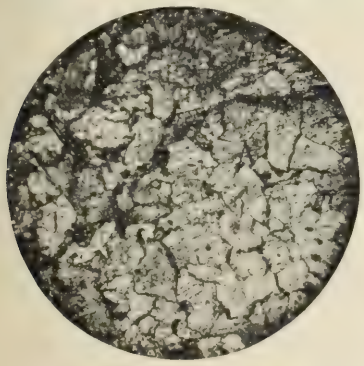


FIG. 3 × 120.

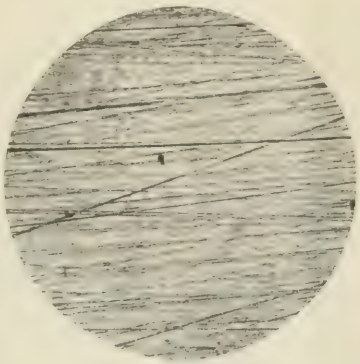


FIG. 4 × 120.

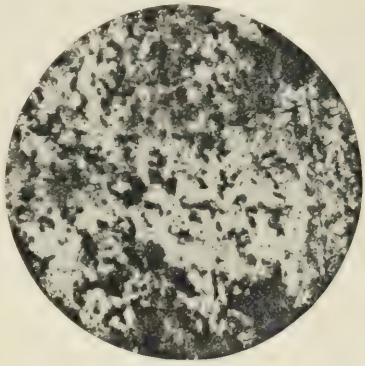


FIG. 5 × 120.

While temperature has great influence on the development of rust in these experiments there are other influences which affect the results.

The purity of the metal determines to a great extent the rate and amount of corrosion. This is definitely indicated in my experiments. Of the impurities in steel, manganese seems to have the greatest influence on the rate of corrosion. My experiments are not exhaustive enough to warrant any sweeping conclusions regarding the influence of manganese, but as far as they go they strongly indicate that this element is an accelerator of corrosion. This is by no means new. For years, metallurgists and other scientists have held the opinion that manganese is the chief instigator of corrosion. Of this, however, there can be no doubt: *The purer the iron the more it will resist corrosion.* I believe I am justified in drawing this conclusion from my experiments. Indeed it follows directly from the electrolytic theory of corrosion, and the great majority of scientists hold this opinion.

Friend's apparatus is an ingenious device for investigating the corrosion of iron and steel in a pure electrolyte, *e. g.*, water containing only dissolved air, free from all traces of acids or bases. Since corrosion in a pure electrolyte is very probably the true starting point, much can be learned by using this apparatus. The conditions of the experiment are ideal since only the three substances concerned—iron, air and water—are brought in contact; no soluble matter coming from glass vitiates the experiment.

No theory ever advanced to explain the corrosion of iron has been so satisfactory as the "electrolytic" theory, announced by Dr. Whitney, and so ably championed by Drs. Walker and Cushman. Practically all known facts connected with corrosion are explained in the light of this theory. The "acid" theory explains many phenomena of corrosion, but it is narrow in its application and, after all, is only a special case under the general electrolytic theory. When carbonic acid enters the pure water electrolyte, it greatly increases the number of hydrogen ions, and, in addition, pollutes the electrolyte with CO_3 ions. The solution pressure of the metal is thus greatly ncreased and corrosion is accelerated.

Acids are only accelerators of corrosion. They are not the cause. The true starting point of corrosion is the solubility of iron in pure water, its electrolytic solution pressure. This property was given iron by nature, and with all our controversy we cannot take away that which nature gave.

GENERAL CONCLUSIONS.

1. Part 1 of each experiment confirms Friend's statement that iron or steel *will not* rust in pure water and air combined. *The failure of the metals to rust, however, was entirely due to temperature conditions and to rapidly changing pure water.*

2. Expts. No. 1, 2, 3, 6 and 8, Part 2, prove conclusively that pure iron or steel *will* rust in pure water and air combined, provided the temperature of the metal and pure water is not below 22° C., and provided the same water remains for a sufficient time on the metals.

3. Exp. No. 4, Part 2, proves that rust is developed rapidly if the temperature of the metals and pure water is about 55° C.

4. Expts. Nos. 5, 7 and 9, Part 2, prove that still further increase in temperature results in a decided increase in the rate of corrosion.

5. Exp. No. 10, Part 2, demonstrates that the *same pure water* may remain on the metal for an indefinite period, and no rusting takes place, provided the temperature of water and metal is sufficiently low.

6. With my modification of Friend's apparatus, equally good results are obtained by using either barium hydroxide, or potassium hydroxide. Barium hydroxide is to be preferred since it is not as liable to render the metal passive.

7. In general, pure iron or steel will rust in pure water and air combined, free from all traces of acids. The amount of rust produced is a function of the temperature and of the purity of the iron.

8. The "acid" theory of corrosion is untenable.

9. All phenomena observed in these experiments are in perfect harmony with the electrolytic theory.

10. The electrolytic theory of corrosion is further confirmed by these experiments.

THE RELATIVE CORROSION OF IRON AND STEEL PIPE AS FOUND IN SERVICE.[1]

By William H. Walker.

Received February 5, 1912.

There are few subjects relating to the corrosion of metals which have received so much attention, or around which there has centered so spirited a discussion, as the relative merits of iron (meaning thereby wrought iron) and steel. The fact that this matter is one still receiving attention, notwithstanding the great volume of accumulated and available literature, is due to a number of causes, among which may be mentioned: First, that although the words "iron" and "steel" carry with them a definite idea as to general methods of manufacture and some of the more easily discernible properties, they convey no idea as to standards of value. It is possible to make very poor iron and very good steel, and it is just as possible to make the reverse. Hence when an investigator compared the corrosion of a poor iron with a good steel, he obtained results which favored steel; when the material under study was the reverse, iron was shown to be the more resistant metal. Second, there is a woful lack of uniformity of conditions obtaining in many, if not most of the experiments which have been carried on for the purpose of comparing resistance to corrosion. Some specimens were large, some small; some cleaned of scale, others not; some immersed in deep water, others in shallow water; etc., etc. The corrosion of iron is so sensitive to changing conditions of surface, oxygen concentration, salts in solution, and the like, that only when the most careful preparation is made to maintain all conditions

[1] Abstract of a paper read before the New England Water Works Association, Dec. 13, 1911.

constant, is a comparative test of value. We will not discuss these conditions here, but take pleasure in referring the reader to that most excellent book on "The Corrosion of Iron" by Dr. J. Newton Friend,[1] where a complete treatment of the general subject will be found. Third, many times opinions are formed and expressed by the casual observer which fail to take into consideration not only the fundamental conditions necessary to accurate comparative work, but also less obvious conditions which make a comparison unreliable. For example, a person may notice the rapid rusting of a cheap grade of steel wire fencing which had originally but a wash of zinc as a substitute for galvanizing, and thus become suspicious of the durability of all steel. Or he may notice holes in a metal roof put up in place of a material known to have lasted a much longer time than the new roof. He concludes that the latter is of less value without having any knowledge of the change of conditions in the locality, class of metal and the thickness of the new roof, nature and thickness of the galvanizing or other protective coating and so forth.

Owing to the proverbial conservatism of New England the introduction of steel pipe has been slower in this territory than in other parts of the country. There is a tendency to pronounce any pipe which withstands corrosion as being wrought iron, while the fact that a pipe corrodes easily is considered by many proof in itself that it is steel.

To determine what the facts actually are in regard to the relative life of service pipes which have been in constant use for a number of years throughout New England, an investigation was undertaken in which it was proposed to seek out instances where steel and iron pipe had been used together in the same system; and further, where the two kinds of metal were separated in this system only by a coupling. Any influence which the coupling might have would be present equally with the iron and with the steel, while conditions of oxygen concentration, temperature, pressure, flow of water or steam, etc., would be as nearly identical for the two kinds of metal as it is possible to obtain. It was intended also to collect in this way material of known resistance or tendency to corrosion, in order to further test the applicability or truthfulness of the so-called "acid corrosion test." While the majority of the pipe so obtained was from hot and cold water feed systems, enough were selected from live and exhaust steam lines, hot water and steam heating systems, etc., to make the conclusions drawn of general application. The investigation was necessarily tedious in that each pipe had to be examined to determine whether it was of iron or steel, and many instances were found that would have served our purpose well, but where it was impossible to remove the pipes from the system. The pipes were sent to the laboratory where they were each split lengthwise into two halves and carefully cleaned from scale and rust by soaking in an ammonium citrate solution, with an occasional brushing. In this way the scale and rust were removed without dissolving any of the iron. An estimation of the extent of corrosion was made by measuring with a micrometer gauge the ten deepest pits per unit distance of length. I give the measurement of those samples of pipe which were rusted to practical destruction, that is, where either the iron or the steel showed pits over one tenth of an inch in depth.

[1] "The Corrosion of Iron and Steel," by J. Newton Friend. Longmans, Green & Co., New York.

	Depth of pitting.		
Sample number.	Mean of ten deepest pits. Inches.	Deepest pit. Inches.	Least of ten deepest pits. Inches.
W-10—Iron	0.102	0.134	0.085
W-11—Steel	0.075	0.095	0.067
W-22—Iron	0.114	0.160	0.068
W-23—Steel	0.075	0.107	0.042
W-24—Iron	0.139	0.168	0.109
W-25—Steel	0.140	0.204	0.076
X-15—Iron	0.077	0.101	0.069
X-16—Steel	0.040	0.047	0.034
X-29—Iron	0.042	0.060	0.030
X-30—Steel	0.066	0.103	0.042
X-49—Iron	0.077	0.113	0.049
X-50—Steel	0.071	0.122	0.040
X 57—Iron	0.038	0.110	0.012
X-58—Steel	0.026	0.053	0.012
X-69—Iron	0.113	0.159	0.032
X-70—Steel	0.119	0.177	0.095
X-71—Iron	0.115	0.169	0.063
X-72—Steel	0.075	0.156	0.042

The results are a splendid vindication, also, of the principle that if oxygen be excluded from water, no corrosion will take place. When the water in the lines examined was stagnant, as in fire sprinkler system for buildings, or in lines where the water was circulated over and over again without exposure to the air, as in some hot water heating systems, no corrosion was to be observed. On the other hand where fresh water was constantly added to the system, and heated within the system, corrosion was very rapid and in some cases excessive.

We were able to get sixty-four comparisons of iron and steel where the history of the installation was known. The results are as follows:

Comparison where iron was found more corroded than steel	20
Comparison where steel was found more corroded than iron	18
Comparison where steel and iron were equally corroded	9
Comparison where corrosion was negligible	17

These results again demonstrate that taken *on the average* there is no difference in the corrosion of iron and steel pipe. Conversations held with the engineers in charge of plants during this investigation confirm the statement already made that a pipe is frequently called steel when corrosion is found to be excessive, while it is set down as iron if it rusts but little.

In order to get some measurement of the influence of oxygen in the water of the modern hot water supply system a relatively large scale experiment was carried on at the plant of the Walworth Mfg Co. in South Boston. Two coils made up from pieces taken from the same length of pipe were each fed with water from the same source at the same temperature. In one case the water was heated to 85° C. in an *open*

tank, while in the other the water was heated to the same temperature in a *closed* tank. The feed water contained on the average 5.85 cc. of oxygen per liter, and passed through each coil at the rate of one half gallon per minute. After running 1750 hours the coil fed with water heated in an open tank had lost 22 grams, while the coil fed with water heated in a closed tank had lost 155 grams. In neither case was the oxygen completely removed; if the water in the open tank had been gently *boiled*, corrosion in the coil fed with this water would have been entirely prevented.

In order to show what relation may exist between the so-called acid corrosion test and the real corrosion as found in service, eleven pairs of iron and steel were selected and subjected to 20 per cent. sulfuric acid for four hours at room temperature. Four pairs were selected in which the steel was decidedly better than the iron in service, four in which the iron had shown decidedly better than the steel, and three in which there was no difference between the two metals.

In six instances the relative corrosion as shown by the sulfuric acid test corresponded with the corrosion as found in service. In five instances corrosion as shown by the acid test was exactly contrary to that found in service. Although the greatest care was taken to have the specimens of the same size, cleaned in the same way, and in the same physical condition, the results show that no reliance can be placed in this accelerated acid test, but that it may be entirely erroneous and very misleading. Not only did the acid test not agree with service test when steel was compared with iron, but the steels failed to agree among themselves, and the irons showed no agreement when considered by themselves.

I wish to express my appreciation of the work of Messrs. James J. Wilson and Francis Worcester, assistants in the laboratory, without whose aid this investigation could not have been made.

RESEARCH LABORATORY OF APPLIED CHEMISTRY,
MASS. INST. OF TECHNOLOGY,
BOSTON, 1912.

DESCRIPTION OF THE EXPLOSION TEST AT THE EXPERIMENTAL MINE OF THE UNITED STATES BUREAU OF MINES, FEBRUARY 24, 1912.[1]

By GEORGE S. RICE.

Received March 11, 1912.

On the morning of the 24th of February, 1912, there was conducted at the Experimental Mine, near Bruceton, Pa., the 14th and last of the first series of such explosion tests.

The mine consists of a pair of entries in the Pittsburgh seam, about 750 feet long from the outcrop opening to the face. These entries are connected by three cross-cuts; in the first of these from the mine mouth, was a reinforced concrete stopping, the behavior of which in the explosion was one of the points of interest, since the stopping was built of a known strength, 100 to 150 pounds to the square inch. The second cross-cut had a 15-foot sand bag stopping supported by a timber frame. The third cross-cut was allowed to remain open so that the ventilating currents could pass through it. The fan was located at the end of an external 120-foot steel galley leading into a passageway lined with reinforced concrete which in turn entered the air course of the pair of entries above described. The fan at the time of the explosion acted as a blowing-fan: the air entering the air course passed to the last cross-cut, then into the main entry, thence returning on the main entry to the outside. The outer 200 feet of this entry is lined with reinforced concrete. For recording pressures, the velocity of the pressure wave, and the velocity of the flame wave, instruments were placed at stations 100 feet apart. The wiring connecting the stations is intricate, there being 34 separate wires in the cable which led from the face of the mine through the different stations to the outside, and thence to the bomb-proof observatory which contains some of the recording instruments. This is also the control or firing station. The entries or passageways are about 7 feet high and 8 to 9 feet wide, the usual dimensions in mines in the Pittsburgh bed.

The principal object was to determine how and why coal dust explodes, in order that means for prevention and limitation might be suggested from the experiments and tried out subsequently. For the purpose of understanding the nature of coal dust explosions and for the comparison of different remedies, instruments were provided, as without instruments it would not be known whether the checking or prevention of the dust explosion was a matter of accident or otherwise. In order to obtain consistent results, the coal dust employed in the tests had to be of known kind and size and distributed evenly. To accomplish such distribution, shelving three inches wide was placed along the walls with the coal dust on these. In the test of February 24th, one pound per linear foot of entry was used on the shelving with one pound per linear foot on the floor of the entry. In the previous public demonstration and explosion on October 31, 1911, one pound per linear foot had been used on shelves, but none on the floor. In other words, in the explosion of February 24th, double the quantity was used.

The real consideration in loading was the amount per cubic foot of space, since a limiting influence in any explosion is the quantity of oxygen available for the combustion. If the coal dust is completely burned, only 12/100ths of an ounce is required to use up all the oxygen in a cubic foot of air. As a matter of fact, there is rarely complete combustion; usually there is a considerable amount of fixed carbon not consumed. The gases distilled from the coal are thus chiefly brought into play. When the loading is two pounds per linear foot there is about 64/100ths of an ounce of dust per cubic foot of air or five times that which is theoretically necessary to use up all of the oxygen.

The coal dust loading in the main entry extended from the mouth to the face. The loading was also continued through the last cross-cut into the air course and out same for 200 feet. At this point there was

[1] Printed by permission of the Director, United States Bureau of Mines.

a Taffanel stone dust barrier, consisting of a group of 13 shelves about five feet apart center to center, placed across the passageway about five feet above the track. Each shelf consisted of two one-inch boards, 10 inches wide, making the total width of a shelf 20 inches, on which finely ground stone dust was placed: there were about $2^1/_2$ cubic feet, or about 200 pounds, of stone dust on each shelf. This style of barrier has been particularly developed by M. Taffanel at the Liévin, France, testing station, where, in an external gallery, it has proved very effectual in arresting coal dust explosions. The system has been generally adopted in French coal mines.

Beyond the barrier of stone dust there were 50 feet more of coal dust loading. Small tufts of loose guncotton (loose guncotton is inflammable but not explosive) were placed at intervals throughout the mine, in addition to the flame circuit breakers in the main entry, to determine the extent of the flame.

The initiation of the explosion was at the face of the main entry, by a single blown-out shot of three pounds of black powder stemmed with 5 inches of fire-clay. In order to insure that the shot would blow out, the hole was cased with $1^1/_2$ inch pipe. A similar hole was prepared in case of failure of the first, but was not fired. The shot was ignited by an electric detonator connected through the cable with the observatory. The wires of the flame circuit breaker were placed immediately in front of the hole so as to obtain a record of the moment the flame started from the cannon.

EXPLOSION AND THE RESULTS.

After the party of mine inspectors and others interested in mining had inspected the mine, Mining Engineer L. M. Jones and Mine Foreman Howarth connected up the fire lines, no one else being in the mine. Then having spread some coal dust in front of the holes, they came out of the mine. A locked switch at the outside and a similar locked switch in the observatory were thrown in to complete the firing line. All was then ready for pressing the button. The visitors having assembled at vantage points where they would be safe, the boiler plant whistle was blown and three minutes afterward the button was pressed. Two and a half seconds later, as shown by the records, a black cloud of dust shot out of the main entrance accompanied by a tongue of flame and a violent detonation occurred. The smoke from the entrance increased in volume for a few seconds and then a reverse current, caused by a vacuum in the mine, set in and the smoke did not again come out for a number of minutes after the ventilation had been reëstablished by hanging brattices across the air course and over the conduit openings. The flame did not issue from the air course and a later investigation of the tufts of guncotton showed that it had not come closer than 60 to 75 feet from the mouth. It seems probable that the non-appearance of the flame at the mouth of the air course or any extreme violence, was due in part at least to the Taffanel stone dust barrier. This was smashed to pieces, as would be expected in opposing so violent an explosion, but this effect is what was desired as it threw into the explosive wave a large mass of finely divided dust which was intended to cool the flame. From the point where the explosion originated in the face of the main entry through the last cross-cut and through the barrier, a distance of 340 feet, the explosive force was sufficient to throw down the upper two feet of the sand-bag stopping in the second cross-cut. The flame penetrated through the barrier. In spite of the considerable violence shown at the barrier, there was practically no violence shown beyond it. It may be well to state here that some previous tests were made in which the barrier was closer to the origin of the explosion and in these cases the flame was always extinguished while passing through the barrier.

THE EFFECTS OF THE EXPLOSION IN THE MAIN ENTRY.

The shot which caused the ignition had blown out a small crater in the coal in spite of the pipe linings which had been broken open; except within a few feet of the shot there was little violence for a considerable distance, but there was much evidence of flame in the last cross-cut. At the second cross-cut in which there was the second sand-bag stopping, the upper two feet were thrown down, the first part of the bags towards the air course, and the upper part toward the main entry. Probably the first effect was from the explosion in the main entry and the second was due to the explosive wave in the air course, which, with the added length of the last cross-cut, had a longer distance to travel. Beyond the middle cross-cut, the shelving, made of 3 × 4 inch hardwood timber, in many places was displaced and in some places broken. The track ballast in some places was lifted, evidently by the depressive wave, or vacuum, following the explosive wave. The violence increased in going out, in the neighborhood of station 150, the concrete arches having been lifted in several places, breaking the face of the concrete and exposing the arched iron reinforcement (3/4-inch square rods). At this station the manometer indicated a pressure of over 110 pounds per square inch—this pressure being measured at right angles to the explosive waves would therefore be considered static pressure. The pressure at the station fifty feet from the mouth was less than that at station 150. Outside the mine the gates were recessed behind concrete buttresses and these were carried bodily away. Fifty feet outside the entrance there had been an empty car. This was thrown to the opposite side of the ravine, a distance of 200 feet.

The pressure circuit breakers and the flame circuit breakers indicated that the explosion traveled quite slowly at first but rapidly increased in velocity going outward, showing a speed of over 2083 feet per second obtained between stations 450 and 350 and also between stations 350 and 250. Beyond this the circuit breakers failed to work. An interesting fact in connection with the recording of the velocities of the advance wave and the flame was that the flame, while much behind the advance wave at the start, caught up rapidly with it as the entrance was reached.

CONCLUSIONS.

As a demonstration the experiment was less spectacular than that of October 31, 1911, as on that occasion the flame burst from all the openings, whereas in the experiment of February 24th the flame appeared only at the main entrance. Also, it did not spread so widely as in the previous demonstration. There was a quick flash projected through the center of the cloud of dust. In the explosion of October 31, 1911, the manometers did not have springs strong enough to indicate the pressures, which difficulty had been removed on February 24th, so that a pressure of over 110 pounds was shown by the manometer at station 150. The detailed information obtained from the various readings will appear in a publication of the bureau on the work of the Experimental Mine.

As regards the efficiency of the Taffanel barrier the evidence is not conclusive. The flame was not immediately extinguished by the barrier, but traveled 200 feet farther; nevertheless, without the barrier, it is probable that, with the large amount of dust being carried from the loading farther in, the flame would have gone to the entrance. This is the more probable since the violence shown by the smashing of the barrier indicates that the explosion had attained considerable violence at this stage. It is intended to make systematic tests of such barriers in the next series of tests.

THE EXPANSION COEFFICIENT OF GRAPHITE.

By Arthur L. Day and Robert B. Sosman.

Received March 9, 1912.

As a basis for the measurement of the specific volumes of silicates at high temperatures we found it necessary to know approximately the expansion coefficient of Acheson artificial graphite up to 1600°. The published data on graphite are so inconsistent and cover so small a temperature range that we redetermined this constant over the range from 0° to 1500°; the results obtained form the material of the present paper.

The expansion was measured directly on a bar 3 mm. by 5 mm., by 700 mm. long, with a comparator which has been used in this laboratory for measuring the expansion coefficients of alloys of platinum with rhodium and iridium.[1] The comparator consists of two micrometer microscopes held at a fixed distance of 500 mm. apart by invar bars; upon this system is mounted another invar bar by which any changes in this fixed distance amounting to 0.001 mm. or more can be detected.

Two points on the graphite bar, 500 mm. apart, were marked by flattened pieces of platinum wire bound around it, each having a fine line cut at the middle of the wire. The bar was heated by sending a heavy current through it, and a uniform temperature along its length was obtained by slightly adjusting its thickness. It was surrounded by a tube of Marquardt porcelain, and this again by a wide glass tube, each free to expand independently of the bar. The space within the tube was kept filled with carbon monoxide. The apparatus is shown in plan and section in Fig. 1.

In the reducing atmosphere a thermoelement could not be used. The temperature was, therefore, found by noting the melting point of small fragments of aluminum (658°), silver (960°), copper (1083°) and the mineral diopside (1391°), lying upon the bar. Intermediate temperatures were read by means of a Holborn-Kurlbaum optical pyrometer, which thus served simply as a device for interpolating between the melting points. It was not necessary to obtain great accuracy in the temperature measurement, as the expansion is small.

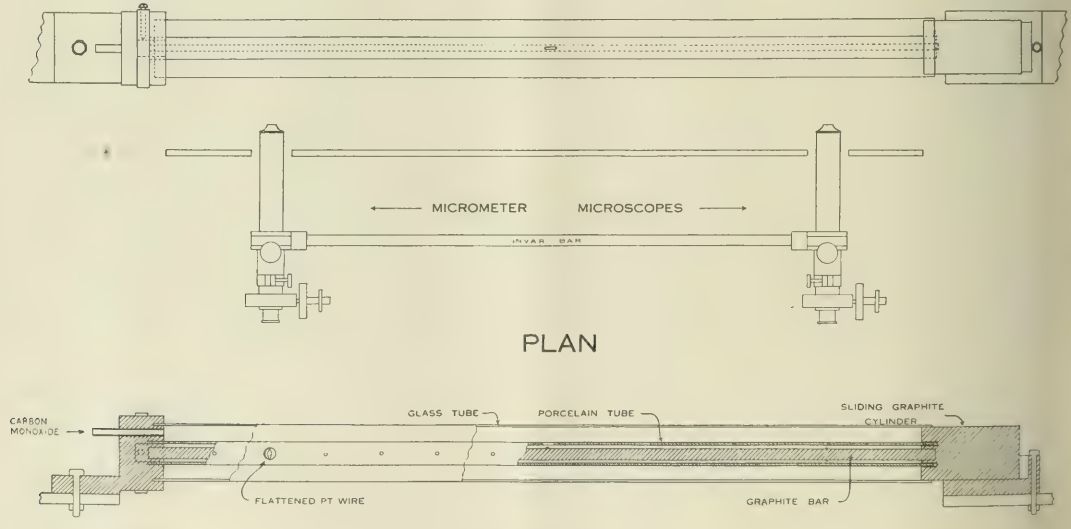


Fig. 1. Apparatus for Determining the Expansion Coefficient of Graphite.

Below 700° the expansion is so small that we found

[1] Day and Sosman, *Am. J. Sci.*, **26**, 425–436 (1908); **29**, 111–114 (1910); *Carnegie Pub.*, **157**, 27–36, 61–63 (1911).

necessary, in order to obtain accurate measurements of the coefficient, to use the method which we had previously employed for the platinum alloys: namely, to heat the bar in a narrow tubular resistance furnace, and read the expansion on a series of very fine lines 0.2 mm. apart, drawn with a dividing engine. These lines were drawn upon the polished ends of small plugs of silver or platinum set into the graphite at points 500 mm. apart. Up to red heat (700°) the bar could be protected fairly well against oxidation, and contamination of the thermoelement could be prevented by enclosing it in Jena glass capillaries.

Table I contains the data. In the first two columns are given the date and the temperature at the time of the measurement. In the third column is the initial distance at 0°, between two reference lines on the silver or platinum markers on the graphite bar, in mm.; this distance was frequently changed slightly by resetting the silver or platinum markers. The fourth column contains the expansion from 0°, in mm., and the fifth, the mean linear expansion coefficient ($\Delta l/l_0 t$) from 0° to t°. The coefficient is plotted against temperature centigrade in the curve of Fig. 2.

The coefficient is seen to be very small, though increasing rapidly with rising temperature. The total expansion up to 1000° is only about one-fifth of that of platinum. Two samples of graphite were used, but no systematic difference exceeding the error of measurement was observed.

The greatest uncertainty arises from permanent changes in length of the bar during heating. In every case where the change was measurable, the bar was longer than before heating, as if this somewhat porous material had failed, after expanding, to entirely pull itself together again. The largest change noted was 0.046 mm., which is 0.009 per cent. on the total length, and therefore quite negligible when the total length or volume is being considered.

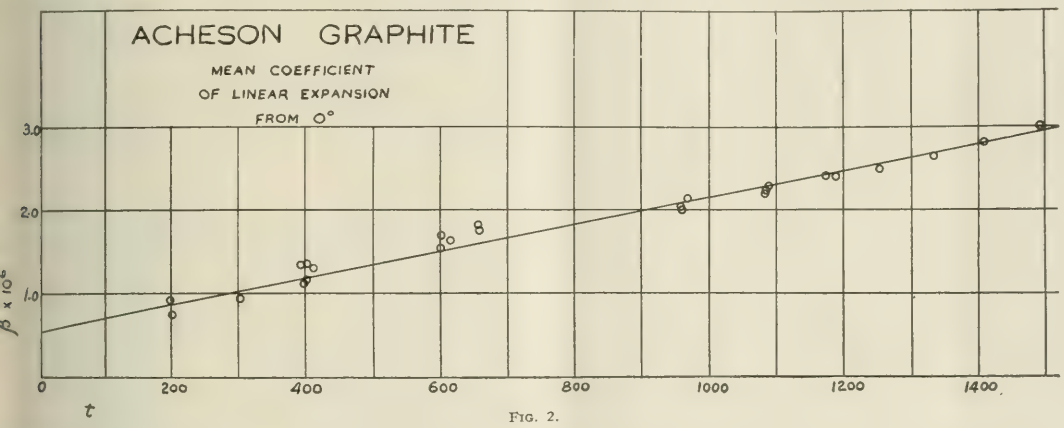


FIG. 2.

Within the limits of error, the results may be expressed by the formula

$$10^6\ \beta = 0.55 + 0.0016t$$

in which β is the mean linear coefficient $\left(\frac{\Delta l}{l_0 t}\right)$ from 0°. The "true coefficient" α, or rate of expansion $\left(\frac{1}{l_0}\cdot\frac{dl}{dt}\right)$ at any temperature t would be therefore:

$$10^6\ \alpha = 0.55 + 0.0032t.$$

If this equation continues to hold below 0°, the true coefficient would become zero at about —170°; in other words this would be the temperature of maximum density. According to Fizeau's measurements, diamond has a similar point of maximum density or zero expansion at —42°.

The published figures on the expansion coefficient of graphite vary widely. We do not know of any previous determinations on Acheson graphite, nor have the manufacturers a record of any. The following data have been obtained on natural graphites:

Source.	Observer.	Range.	$\beta \times 10^6$.
"Batougol" (Siberian) graphite	Fizeau[1]	10° to 85°	$7.45 + 0.0051t$
"Siberian" graphite	Muraoka[2]		3.8
"Cumberland" graphite	Dewar[3]	At —190° (from 17°)	24.4

[1] *Compt. rend.*, **68**, 1125–1131 (1869). *Pogg. Ann.*, **138**, 26–31 (1869). Fizeau's values are for α, the true coefficient; we have calculated the mean coefficient from 0° from the original values.

[2] *Ann. Physik*, **13**, 307–318 (1881).

[3] *Proc. Roy. Soc. London*, **70**, 237–246 (1901).

TABLE I.—OBSERVED EXPANSION OF ACHESON GRAPHITE.

Date.	t.	l_0.	Expansion from 0° to t°.	Mean linear expansion coefficient $\times 10^6$.
		I. Self-heating Bar.		
Dec., 1910.	658°	499.94	0.60	1.82
"	658		0.58	1.77
Dec.	970	500.16	1.04	2.14
"	1085		1.21	2.23
Dec.	960	500.11	0.98	2.05
"	1085		1.19	2.20
"	1175		1.42	2.41
"	1255		1.56	2.49
Dec.	960	500.13	0.97	2.02
"	1090		1.25	2.29
"	1190		1.42	2.40
"	1335		1.77	2.65
"	1410		1.98	2.82
"	1495		2.25	3.02
		II. Platinum Resistance Furnace.		
n., 1912.	198	500.974	0.090	0.91
"	396		0.265	1.34
an.	202	501.020	0.075	0.74
"	401		0.228	1.13
an.	304	501.016	0.145	0.95
an.	401	501.433	0.229	1.14
"	602		0.467	1.55
an.	403	501.279	0.274	1.35
"	604		0.514	1.69
eb.	413	501.291	0.272	1.31
"	616		0.506	1.64

For pencil-graphite, Muraoka found the value 0.95×10^{-6}. But as this is a mixture containing only 52 per cent. of graphite, this value is hardly comparable with data on pure materials.

The wide range of these data is striking, especially when taken in comparison with the expansion coefficients of other forms of carbon, and of carbon compounds. It will be seen from the following table that from the expansion coefficient of diamond to that of anthracite we have an increase of forty-fold.

Form.	Observer.	Range.	$\beta \times 10^6$.
Diamond	Fizeau[1]	10° to 85°	$0.60 + 0.0072t$
Arc carbons (of coke)	Muraoka		0.32
Arc carbons	Muraoka		1.5
Arc carbons	Muraoka		2.05
Arc carbons	Muraoka		3.0
Gas carbon (retorts)	Fizeau[2]	10° to 85°	$4.96 + 0.0055t$
Anthracite (Pennsylvania)	Fizeau[2]	10° to 85°	$24.02 - 0.0408t$
Coal (Charleroy)	Fizeau[2]	10° to 85°	$26.63 + 0.0148t$

These relations are shown in another form in the curves of Fig. 3, in which the mean coefficient of cubical expansion from 0° is plotted against temperature. Coefficients calculated from the data of Joly[3] on the expansion of diamond to 750° are included in the curves. It is worth noting that at 0° the expansion coefficient of Acheson graphite and of Fizeau's diamond are practically the same.

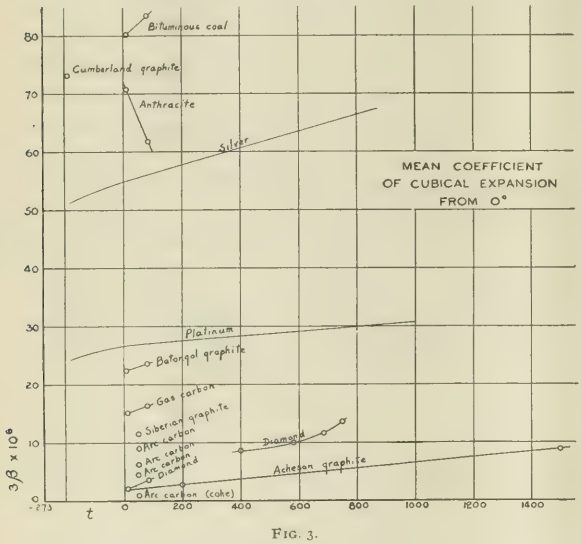


FIG. 3.

A rough parallelism is immediately evident between the temperatures of formation and the expansion coefficients of the different varieties of carbon in the two tables above. The highest coefficient is possessed by bituminous coal, which is followed closely by anthracite. The Cumberland (Borrowdale, England) graphite investigated by Dewar stands next in order, and very near anthracite. This graphite has been formed in company with intrusions of igneous rock into clay-slates containing organic matter. The purer and better crystallized Batougol graphite, with a lower coefficient, occurs in veins in granite and syenite.[4]

Various samples of arc light and retort carbon, all of which probably have been heated in the process of manufacture to a higher temperature than any of the natural graphites, stand next in the order of decreasing expansion. Lowest of all (excepting one sample of arc carbon made of coke) come diamond and Acheson artificial graphite. The formation temperature of diamond is unknown. The artificial graphite is made by heating anthracite, petroleum coke, etc., to a temperature above 2200°.[1]

The view has been repeatedly expressed, by Moissan,[2] Luzi,[3] and others, that none of the three forms of carbon as at present distinguished, not even diamond, can be looked upon as a substance of fixed and reproducible properties, comparable for instance to the monoclinic and rhombic forms of sulfur. In the case of graphite, there are wide variations in such physical properties as density and electrical conductivity, as well as in chemical properties such as combustibility and the formation of "graphitic acids" of widely varying composition when different kinds of graphite are treated with nitric acid and potassium chlorate.

If we look upon natural graphites as products of metamorphism from organic matter, whether by the direct action of heat alone or through the medium of solutions, we may imagine the complicated carbon chains and rings of the compounds that make up bituminous and anthracite coal as persisting after the removal of their hydrogen and oxygen, giving a whole series of "graphites" whose properties change progressively as the molecules become simpler. Berthelot held this view as regards amorphous carbon.

Arsem,[5] as a result of his studies on the graphitization of different forms of "amorphous" carbon, and the densities of the resulting products, reaches this tentative conclusion: "Graphite in the most restricted sense of the term is an allotropic form of carbon having a definite and perhaps not very complex molecular configuration... When an organic compound is decomposed, there results a mixture of substances constantly increasing in complexity until finally carbon is obtained. This carbon need not be regarded as a simple substance, but may be considered to be a mixture of many varieties of carbon each with a different number and arrangement of atoms in the molecule... In a given sample of amorphous carbon some of the molecules will be capable of easily undergoing rearrangement under the influence of heat to form graphite molecules, while others will not, and the proportion of molecules capable of such change will determine the character of the final product."

Arsem's definition is as follows: "Graphite is the allotropic form of carbon having a specific gravity of 2.25–2.26." This is the specific gravity of Acheson graphite, and all the graphites made by Arsem were equal to or less than this. "Those varieties of carbon which have some of the physical properties of graphite

[1] *Pogg. Ann.*, **128**, 583 (1866).
[2] *Compt. rend.*, **68**, 1125–1131 (1869).
[3] *Trans. Dublin Soc.*, [2] **6**, 283–304 (1897).
[4] Donath, "Der Graphit," **1904**.
[1] Gillett, *Jour. Phys. Chem.*, **15**, 302 (1911).
[2] *Chimie Minérale*, **1905**, II, 222.
[3] Donath, "Der Graphit," **1904**, 11.
[4] *Ann. chim. phys.*, [4] **9**, 475 (1866).
[5] THIS JOURNAL, **3**, 799–804 (1911).

h as color, softness, and streak, but a lower specific gravity, may perhaps be regarded as impure phites; that is to say, mixtures of graphite with ier forms of carbon."

Against the view set down in preceding paragraphs, at so-called graphite is not a simple and reproducible bstance, we have the recent work of LeChatelier d Wologdine.[1] They found that the density of heson graphite and of five natural graphites, after rification to remove ash and compression to drive t air, was 2.255, and conclude that this property ines graphite as a simple and reproducible subnce. But it should be noted that their process of rification involved fusion at a red heat with potash, reatment which might produce profound changes in e graphite itself.

In conclusion, the wide divergence in expansion coefient which we have noted above seems quite beyond the range of possible experimental error, and dicates some fundamental difference between these rious graphites.

Geophysical Laboratory, Carnegie Institution, Washington, Mar., 1912.

VOLUMETRIC METHOD FOR THE DETERMINATION OF THORIUM IN THE PRESENCE OF OTHER RARE EARTHS. THE ANALYSIS OF MONAZITE SAND.

By F. J. Metzger and F. W. Zons.

Received February 13, 1912.

When an excess of ammonium molybdate solution added to a solution of a thorium salt under proper nditions of temperature and acidity, thorium is antitatively precipitated as molybdate. Other rare rths, such as cerium, lanthanum, neodymium, praseomium, erbium, yttrium, gadolinium, etc., give no ecipitation whatever under similar conditions.

The above facts, observed by one of us some years o, forms the basis for the method described in this per.

The thorium molybdate precipitate is somewhat latinous in character, pale yellow in color, and sets very slowly. In our earlier experiments an atmpt was made to filter off the precipitated thorium d make the determination gravimetrically, but ing to the slimy nature of the precipitate, filtration d washing were impossible.

The usual indicators for molybdenum were tried h the hope that a direct titration of the thorium uld be made, but without success.

Cazeneuve[2] found diphenyl carbazide to be a sensitive reagent for certain metallic salts, as those of copper, mercury, iron and also for chromates. Lecoq[3] used an alcoholic solution of diphenyl carbazide as a test for molybdenum. A pink coloration is produced, but the author states that the test is more sensitive after the solution of diphenyl carbazide has been allowed to stand for some time. In order to test the applicability of this indicator, a number of titrations of pure thorium nitrate solution were made, and the results obtained were concordant. The indicator was used "outside" on a white indented tile, the end of the titration being marked by the appearance of a pink coloration which lasts about fifteen seconds. Some experience is required to identify the end point. This is gained in standardizing the ammonium molybdate against a standard thorium nitrate solution. *It is necessary to use a solution of the indicator at least two weeks old*, as the freshly prepared solution requires a considerable excess of molybdenum to produce a pink coloration. The titration is made at room temperature, in the presence of acetic acid.

The solutions used in the experimental part of the work were as follows: *Thorium nitrate*—A solution of pure thorium nitrate accurately standardized by precipitating as oxalate, igniting and weighing as oxide. *Potassium permanganate*—An approximately 0.1 *N* solution standardized against specially prepared Mohr's salt; 1 cc. = 0.005835 Fe. *Ammonium molybdate*—Approximately 20 grams ammonium molybdate per liter. In order that the thorium-molybdenum ratio in the precipitate might be determined, this solution was carefully standardized by acidifying, reducing in a Jones reductor and titrating with permanganate as usual. The average of a number of titrations gave 10 cc. molybdate solution = 28.2 cc. $KMnO_4$. Assuming the reduction to be $MoO_3 \longrightarrow Mo_{24}O_{37}$, then 1 cc. molybdate solution = 0.0098136 Mo. *Indicator*—0.5 gram of diphenyl carbazide[1] dissolved in 200 cc. of 95 per cent. alcohol and allowed to stand at least two weeks before using. The solution when ready for use should be yellowish in color, but show no pink tinge.

In order to obtain uniformity in acidity of the solutions for titration and to have the conditions analogous to those obtaining in the analysis of a monazite sand, a number of determinations were made as follows:

A known amount of thorium solution, or thorium solution with the addition of other rare earths, was placed in a casserole and evaporated to dryness on a water bath. To the dry residue 4 cc. of glacial acetic acid were added, then 300 cc. of water. When the salts were dissolved, the cold solution was titrated with ammonium molybdate. The molybdate solution should be added a few tenths of a cc. at a time, with vigorous stirring after each addition, finally finishing drop by drop. The end point is reached when a drop of the solution produces the previously described pink coloration when brought in contact with a few drops of indicator on a white tile. After a little experience the end point can be determined with great accuracy. The following table shows the results obtained:

[1] A convenient and satisfactory method for the preparation of this compound is as follows: Add 23 grams of phenyl hydrazine to 7 grams of urea in a flask, and heat in an oil bath at 160–170° for six hours, using a reflux air condenser. Allow to cool, add 50 cc. ethyl ether, heat on a hot plate for one hour, decant and add 50 cc. ethyl ether, heating for two hours longer; a white precipitate is obtained, the residue of reagents going into solution in the ether. Decant the ether, dissolve the precipitate of impure diphenyl carbazide in alcohol and reprecipitate by pouring into excess of water; decant the water, redissolve the precipitate in alcohol and pour again into excess of water. Filter on a Büchner funnel, wash and dry at 105°. Yield, 14.3 grams diphenyl carbazide. M. p. 150°–151°. *The diphenyl carbazide is white when just precipitated but in time turns brownish yellow. A trace of impurity causes it to turn pink; hence all vessels, dropping tubes, etc., must be scrupulously clean. The indicator, when on the white tile, should be yellowish or brownish yellow.*

[1] *Compt. rend.*, **146**, 49–53 (1908).
[2] *Ibid.*, **131**, 346 (1900).
[3] *Jour. Chem. Soc.*, **86**[2], 369 (1904).

No.	ThO_2 Gram.	Other earths present	Molybdate solution Cc.
1	0.0500	0	3.68
2	0.0500	0	3.68
3	0.0852	0	6.4
4	0.0852	0	6.4
5	0.0852	0	6.5
6	0.1000	0	7.35
7	0.1000	0	7.4
8	0.0500	0.1 Nd_2O_3	3.9
9	0.0500	0.1 Pr_2O	3.9
10	0.0500	0.1 La_2O_3	3.9
11	0.0852	0.1 La_2O_3	7.1
12	0.0852	0.1 La_2O_3	7.1
13	0.0852	0.1 Pr_2O_3	7.2
14	0.0852	0.1 CeO_2	7.1
15	0.0852	0.1 gram each of Ce, La, Pr, Nd	7.1
16	0.0852	0.1 gram each of Ce, La, Pr, Nd	7.2
17	0.0852	0.1 gram each of Y, Gd, Er	7.2
18	0.0852	0.1 CeO_2	7.1
19	0.0852	0.1 "	7.1
20	0.0852	0.1 "	7.1
21	0.0852	0.1 "	7.1
22	0.0852	0.2 "	7.1
23	0.0852	0.3 "	7.2
24	0.0852	0.3 "	7.1
25	0.0852	0.3 "	7.1
26	0.0852	0.6 "	7.1
27	0.0852	0.6 "	7.1
28	0.0852	0.6 "	7.2
29	0.0852	0.6 "	7.2
30	0.0852	4.26 "	7.1
31	0.0852	4.26 "	7.1

In titrations Nos. 11 to 31, the total dilution varied between 150 cc. and 300 cc., and one gram of sodium acetate was added to each to counteract any possible mineral acid present. These results show that although the consumption of molybdate solution was greater when other rare earths were present, the volume of molybdate was the same whether the added rare earth was small or large in amount. From this it was assumed that the concentration of acetic acid was insufficient to entirely prevent the precipitation of rare earths other than thorium.

Another set of titrations with increased acidity resulted as follows:

No.	Dilution. Cc.	Sodium acetate. Gram.	Acetic acid (glacial). Cc.	ThO_2. Gram.	Other earths.	Molybdate. Cc.
32	300	1	10	0.0852	0	6.4
33	300	1	10	0.0852	0	6.5
34	300	1	20	0.0852	0	6.4
35	300	1	20	0.0852	0	6.4
36	300	1	20	0.0852	0.1 gram each of Pr, La, Nd, Gd	6.43
37	300	1	20	0.0852		6.4

The values here obtained are in satisfactory agreement with those obtained with thorium alone, the increased acidity preventing interference by the other rare earths.

Composition of Precipitate.—Taking the value of the $KMnO_4$ already given (1 cc. = 0.005835 Fe) and its equivalent in terms of molybdate solution (28.2 cc. $KMnO_4$ = 10 cc. molybdate) then 1 cc. molybdate = 0.0098136 Mo. The average of the eleven titrations of thorium alone (Nos. 1–7 and 32–35) gives 0.0815 ThO_2 = 6.095 cc. molybdate, or a ratio Th : Mo = 1 : 2.017. Similarly, the average of titrations 36 and 37 with impurity present gives Th : Mo = 1 : 2.03. It is therefore probable that the precipitate is a normal thorium molybdate.

Analysis of Monazite Sand.—In order to test the accuracy of the method for the determination of thorium in monazite sand, samples of North Carolina and Brazil sands which had been analyzed by the fumaric acid method, the thiosulphate-ammonium oxalate method and the metanitrobenzoic acid method[1] were analyzed.

The volumetric method is carried out as follows: To one gram of the powdered sand in a porcelain crucible is added 10–15 cc. of concentrated sulphuric acid. After several hours heating, the crucible is cooled and the contents transferred, a little at a time and with constant stirring, to about 700 cc. water which has been cooled to near 0°. After standing several hours (over night if convenient) to insure complete solution of the sulphates, the solution is filtered and the residue washed thoroughly with cold water. The filtrate is nearly neutralized with dilute ammonia, 50 cc. of a cold saturated solution of oxalic acid added, and allowed to stand over night. The oxalates are filtered and washed with a dilute oxalic acid solution. When thoroughly washed, transfer precipitate and paper to a beaker, add 20–25 cc. of strong potassium hydroxide solution and heat to boiling. Dilute, filter and wash with hot water. Dissolve the precipitate of rare earth hydroxides off the filter by means of hot, dilute nitric acid. Evaporate to dryness on a water bath. Add a few cubic centimeters of water and again evaporate to dryness to remove free acid. To the dry residue add 20 cc. glacial acetic acid, dilute with 300 cc. water, add one gram sodium acetate and stir until dissolved. Titrate at room temperature with standard ammonium molybdate solution as already described.

The following results were obtained:

	Percentage ThO_2.			
	Volumetric method.	Metanitrobenzoic acid method.[2]	Fumaric acid method.	Thiosulphate ammonium oxalate method.
No. 3 Brazil	4.80	4.76	4.85	4.90
	4.80	4.85		
	4.98	4.99		
	4.99			
	4.99			
	4.99			
	5.05			
	5.05			
	5.05			
Average	4.97	4.87	4.85	4.90
No. 363 Brazil concentrate	5.58	5.60	5.70	5.63
	5.65	5.65		
	5.65	5.67		
	5.65	5.70		
	5.65	5.73		
	5.72			
	5.72			
Average	5.66	5.67	5.70	5.63

[1] For a description of these methods, the reader is referred to the original articles: F. J. Metzger, *Jour. Amer. Chem. Soc.*, **24**, 901. A. C. Neish, *Ibid.*, **26**, 780.

[2] Analyses by this method were made by Dr. A. C. Neish.

	Percentage ThO_2			
	Volumetric method.	Metanitrobenzoic acid method.	Fumaric acid method.	Thiosulphate ammonium oxalate method.
No. 625 Brazil.....	4.85		4.88	
	4.92		4.89	
	4.92			
	4.98			
	5.1			
	5.3[1]			
Average (omitting last).....	4.95			

The following were analyzed by the volumetric method but not checked by other methods:

No. 626 North Carolina.	No. 631 North Carolina.
4.84	5.11
4.84	5.11

CONCLUSIONS.

1. At room temperature thorium is precipitated quantitatively from a cold acetic acid solution (20 cc. glacial acetic acid and 300 cc. water) by means of ammonium molybdate.

2. Other rare earths found in monazite sand are not precipitated under the conditions defined in "1."

3. The ratio of thorium to molybdenum (1 : 2.017 and 1 : 203) indicates that the precipitate is a normal thorium molybdate.

4. By observing proper conditions of acidity, thorium may be accurately titrated by means of ammonium molybdate. Other rare earths have no effect on this titration.

CONTRIBUTION NO. 207, HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY.

THE RESENES OF RESINS AND OLEORESINS.

By CHAS. H. HERTY AND W. S. DICKSON.

Received February 1, 1912.

The oleoresinous exudate of pine trees, commonly called "crude turpentine," consists of a mixture of a volatile oil, acids and unsaponifiable matter. On distillation with steam the volatile oil, "spirits of turpentine," passes off; the residual resin, freed from excess of water by heating, solidifies on cooling and constitutes commercial "rosin." The name "resene" has been applied by Tschirch[2] to the non-volatile, unsaponifiable constituent of such resins and oleoresins.

Though the composition of crude turpentine varies considerably in different specimens, an average analysis of specimens collected by the usual commercial methods would show approximately:

	Per cent.
Spirits of turpentine.....	20
Acids.....	74
Resene.....	6

Resenes, according to their origin, show varying physical states, some being colorless solids while many are very viscous liquids, extremely sticky and non-crystallizable. They are composed of carbon, hydrogen and oxygen, but the per cent. of oxygen is usually smaller than in the accompanying acids. Toward reagents they are very resistant, especially toward alkalies. Although containing oxygen, they show, according to Tschirch,[1] none of the usual reactions indicating the presence of hydroxyl, carboxyl, aldehyde or ketone oxygen, nor are they ethereal salts or lactones. Tschirch inclines to the view that they belong to the class of oxyterpenes or oxypolyterpenes.

While much work has been done upon the volatile oils and the acids of oleoresins, little attention has been paid to the resenes, except ultimate analyses and approximate statements of the proportion present in isolated specimens studied. In connection with an investigation carried out in this laboratory in collaboration with the United States Forest Service, there remained a large number of specimens of resin from well identified individual trees growing in Florida. It seemed desirable, therefore, to study more closely the question of the proportions of resene in these specimens. The investigation was extended to the resins of conifers growing near this laboratory, and to specimens collected in other countries. Finally the amount of resene was determined in several oleoresins obtained in perfectly fresh condition from individual trees in Florida. These specimens were collected from the two species of pines from which crude turpentine is commercially obtained in this country, *Pinus Palustris*, (Longleaf Pine) and *Pinus Heterophylla* (Cuban or Slash Pine).

The resins were prepared by distilling the oleoresins in a current of steam slightly superheated, the temperature being raised to 140° C. toward the end of the distillation. After complete removal of the volatile oil, the residue was kept at 140° C. in the oil bath surrounding the distillation flask until all water was driven off. The molten resin was then filtered through absorbent cotton and cooled to solidification in glass or iron molds.

The determination of resene in the resins was carried out in the usual manner. The weighed specimen, about two grams, was dissolved in a considerable excess of $N/2$ alcoholic potassium hydroxide, allowed to stand at room temperature eighteen hours, diluted with water until separation of the resene began and the solution cleared by the addition of a small quantity of ninety-five per cent. alcohol. This solution was then extracted three times with petroleum ether, boiling below 40°. The combined extracts were shaken out with fifty per cent. alcohol to remove slight amounts of dissolved potassium salts of resin acids. After drawing off the petroleum ether extract into a weighed glass evaporating dish, it was allowed to evaporate spontaneously to constant weight.

In the case of the oleoresins, after spontaneous evaporation of most of the petroleum ether the residue was heated for five hours on a steam bath in order to remove completely the petroleum ether and the volatile oil. Considerable difficulty was experienced at the outset in these evaporations due to the tendency of the material to "crawl" over the rim of the vessel.

[1] The authors are unable to account for this high result.

[2] Tschirch, "Die Harze und die Harzbehäeter," Second edition, p. 1079.

[1] *Loc. cit.*

This was entirely overcome by using a thin coating of vaseline on the rim of the vessel.

The following results were obtained:

TABLE I. PER CENT. OF RESENE IN RESINS FROM DIFFERENT SPECIES.

Species	Local name.	Origin.	Per cent. resene.
Pinus Taeda	Loblolly Pine	North Carolina	4.10
" Palustris	Longleaf Pine	Florida	5.67
" Maritima	Maritime Pine	France	7.37
" Heterophylla	Cuban or Slash Pine	Florida	7.38
" Serotina	Pond Pine	Florida	7.65
" Echinata	Old Field Pine	North Carolina	8.71
" Species unknown		Central America	8.94
" Sabiniana	Digger Pine	California	9.66
" Laricio	Schwarzkiefer	Austria	14.05

In order to test the variation of the amount of resene in trees of the same species two sets of determinations were carried out on trees of different diameters. The results follow:

TABLE II.—PINUS PALUSTRIS (LONGLEAF PINE).

Tree no.	Diameter (inches).	Per cent. resene in resin.
1	7.3	5.26
2	15.0	5.95
3	21.0	9.68
4	13.0	7.45
5	8.7	5.67
6	9.0	5.45
7	13.5	6.22

TABLE III.—PINUS HETEROPHYLLA (CUBAN OR SLASH PINE).

Tree no.	Diameter (inches).	Per cent. resene in resin.
1	7.0	7.87
2	14.5	7.36
3	24.5	7.20
4	12.3	7.25
5	8.2	6.58
6	13.0	7.84
7	9.0	7.00

To determine possible variations in the per cent. of the resene in different seasons of the same year two trees were selected, one each, *Pinus Palustris*, tree No. 2, Table II, and *Pinus Heterophylla*, tree No. 2, Table III. Beginning in the early Spring the oleoresins were collected from these at regular periods of four weeks until the close of the season in the Fall. From the resins prepared from these specimens the following results were obtained:

TABLE IV.

Collection no.	Per cent. resene in resin from Pinus Palustris.	Pinus Heterophylla.
1	5.31	7.36
2	5.44	7.67
3	5.95	7.23
4	6.02	8.17
5	6.09	7.38
6	6.53	7.43
7	5.24	7.77

It is scarcely probable that in the case of *Pinus Palustris* any significance is to be attached to the gradual increase in the per cent. of resene as the season advanced until the last collection.

Further determinations were made of the per cent. of resene in specimens of oleoresin collected with great care in Florida and promptly analyzed. The following results were obtained:

TABLE V.

Tree no.	Per cent. resene in oleoresin of Pinus Palustris.	Pinus Heterophylla.
1	7.10	6.83
2	3.84	6.76
3	7.33	6.96

Finally, a specimen of "scrape" (Gum Thus) was obtained from a Longleaf pine (*Pinus Palustris*). This scrape is the hardened mass which gradually collects on the scarified surface of the tree as a result of the crystallization of the resin acids of the oleoresin. It receives its name from the fact that at the end of the season it is scraped from the surface of the trees by means of a sharp tool. It contains approximately one-half as much spirits of turpentine as the ordinary oleoresin collected from the receptacles. The resin was prepared from this scrape by distillation with steam as above. On analysis it showed 3.14 per cent. of resene.

In continuation of this work, there is now being carried out in this laboratory an investigation of the composition of the resene of *Pinus Heterophylla*.

UNIVERSITY OF NORTH CAROLINA.

A METHOD OF EXAMINING CHINA WOOD OIL.

By PARKER C. MCILHINEY.

Received April 2, 1912.

The examination of china wood oil to determine its quality and to detect the presence of foreign oil presents several difficulties. The iodine figure is not far removed from that of several other oils, the saponification figure is identical with that of many others and although the specific gravity and the refractive index are higher than those of almost any other fatty oil, the difference in these respects from some other oils is not sufficiently great to furnish satisfactory data in all cases.

The most marked characteristic of china wood oil is its property of solidifying readily under the influence of heat or when acted upon by iodine. Heating the oil to a temperature of from 240–280° C. and noting the readiness with which the oil jellies and the consistency of the jelly produced have been extensively used as commercial tests for grading the oil. It is difficult, however, to conduct such a test under conditions which will give numerical values to the results, these being usually stated in terms of the apparent hardness or softness of the jelly, or else in terms of the number of minutes required to jelly at some given temperature. The latter method is open to several serious objections and it is difficult to reproduce in a second experiment the conditions of the first.

The behavior of the oil when iodine dissolved in a suitable solvent is added to it, furnishes a well known qualitative method of identifying china wood oil and particularly of distinguishing it from linseed oil, but since the test as usually carried out gives merely a jelly, no quantitative results are obtainable from them.

It was thought that if this test could be made quantitative so that a separation could be effected between the solidified and the liquid resulting from the action of iodine upon the oil, a valuable and quantitative method of testing the oil might be obtained, particularly as such a test would be directly related to the most important and characteristic property of the oil. A series of experiments conducted with this end in view showed that acetic acid of 99½ per cent. strength or thereabouts was a solvent in which

both the iodine and the oil could be dissolved and out of which the solidified product separated readily so that it might be removed from the liquid portion; furthermore, that this liquid portion could be dissolved in a petroleum solvent boiling under 80° C. while the solid product from the china wood oil was practically insoluble in this solvent. Based upon these facts the following method of analysis was devised:

Weigh into an Erlenmeyer flask about 5 grams of the oil to be examined, add to it 10 cc. of 99½ per cent. acetic acid and after warming it so that there is a perfect mixture of oil and acid, add to it 50 cc. of a solution of iodine in 99½ per cent. acetic acid containing 15 grams of iodine per liter. The acetic acid solution of iodine should be warmed so that when added to the oil solution to be tested it will not chill it. Upon adding the iodine solution there results an almost instantaneous separation of some solid product from the solution in large amount. The solution is allowed to rest for half an hour to insure complete reaction and then 50 cc. of petroleum solvent (b. p. below 80° C.) added and allowed to mix thoroughly with the contents of the flask. The liquid is then drained off from the flask into a separatory funnel and another portion of 50 cc. of petroleum solvent added to the solid residue which has been allowed to remain in the flask so as to wash out of it the residue of liquid products; after pouring off this solvent the solid residue is extracted a third time with 50 cc. of petroleum solvent, the solutions being united in the separatory funnel. Water is now added to the contents of the separatory funnel and this causes a separation of the liquid into two layers, one of petroleum solvent carrying the liquid portions of the reaction in solution and the other of water united with acetic acid. This latter is drawn off and the petroleum solvent repeatedly washed with water till it is free from acetic acid and then shaken out with a solution of potassium iodide to remove free iodine which may be present; after a final washing with water it is transferred to a flask, the solvent evaporated off and the residue weighed. The weight of this residue is a measure of the proportion of those constituents of the oil under examination which are not solidified by the action of iodine.

Broadly stated, the process gives results showing that only a small fraction of china wood oil remains liquid at the conclusion of this process while other oils remain entirely liquid and soluble in the petroleum solvent and if the process be applied to known mixtures of a given sample of china wood oil with soya bean oil the proportion of soya bean oil may be determined with reasonable accuracy. In order to make such a determination, however, upon oils of unknown origin, it is necessary that the per cent. of liquid products which may conveniently be described as "per cent. of soluble iodides" of true china wood oil and also the variation in this per cent. given by different varieties and samples of true china wood oil should be known. In order to investigate this matter it is necessary to obtain a considerable number of authentic samples of such oils and these samples are to be obtained only in China and in the other countries where this oil is produced. The method is, however, submitted as one suitable for the investigation of the oil and particularly as a method for determining the grade of the oil in respect to its most characteristic property.

As the writer has been unable to obtain any considerable number of original small samples of the oil, he refrains from giving the exact figures obtained upon the commercial samples which have been examined but hopes that others may apply the process to authentic samples as they are obtained.

7 East 42nd Street, New York.

ON THE INDICES OF REFRACTION OF CHINA WOOD OIL.

By Louis Elsberg Wise.

Received May 11, 1912.

The increasing use of china wood oil in the paint and varnish industries has created the necessity for a proper examination and standardization of this important article of commerce. Much of this drying oil is sent to European and American ports through Hankow, and a rumor is now current that there have been varied attempts to adulterate these shipments with cheaper products, such as soya bean oil. Whether or not these reports are based on fact, the author of this paper is in no position to decide, but he has found it a proper time to review the recent literature, relating to the characteristic properties of the raw material, and to find, if possible, some method by which the purity of the oil could be gauged.

The important characteristics of the oil[1] are its odor, its peculiar drying properties (in which it differs markedly from linseed), its high specific gravity and its coagulation on heating. The saponification, iodine and acid numbers appear to be of little value in judging the oil.

The jelly which is formed on application of heat is elastic and insoluble in the common solvents. It is ordinarily believed that the gelatinization is due to a polymerization; it is undoubtedly *not* caused by oxygen absorption, and it immediately distinguishes wood oil from the other common drying oils.

Several chemists[2] have recently made a study of the physical characteristics of the "go-back" (the varnish maker's name for this coagulation product), and a number of chemical examinations[3], have been made, which up to the present have led to widely divergent results. A further investigation of the "go-back," as well as the relation between its properties and its technical use, is being made by Mr. Eugene G. Bloch, of our laboratory, and the results of this research may be published at some future date.

Another striking peculiarity of the oil is its high index of refraction. Lewkowitsch states that the refractive index is much higher than that of any other drying oil, and this statement suggested the study of the refractive indices of a number of commercial

[1] Lewkowitsch, *Chemical Technology of Oils, Fats and Waxes*, **2**, 62.

[2] *Private communication.*

[3] *Lewkowitsch*, **3**, 99. Nash, *Private communication to Lewkowitsch.* Norman, *Chem. Ztg.*, **99** (1907).

samples. The data obtained is recorded in the tables given below.*

All attempts to get samples of wood oil of known source and purity were without avail. The difficulty was due to the primitive condition in the collection of the oil and its shipment to the coast from the country districts of China.[1] We received a sample from Mr. Bacon (also purchased on the open market) which is supposed to be a standard, but its source has not been indicated.

The results tabulated below, therefore, represent the refractive indices of *commercial* wood oils shipped to us for use in the manufacture of varnish. The shipments cover a period of approximately eight months, during 1911–1912. Some of them have proved unsatisfactory in the processes of manufacture, and there is some indication that a relation exists between the refractive index and the "working quality" of the oil. That question can be settled only by a far more extended research. Gross adulteration is certainly indicated very clearly and rapidly by the use of the refractometer, and whether foreign oils, present in small quantities may be detected, will depend very largely on the results of future coöperative investigation.

TABLE I.

Mark.	Index of refraction at 25° C.
A.3.20.12	1.5148
A No. 1 A	1.5118
A No. 2 A	1.5130
A No. 3 A	1.5164
A No. 4 A	1.5153
A No. 9A (R. M. S. 3534)	1.5154
A No. 10 A (R. M. S. 3528)	1.5174
S. L. J.	1.5168
Sample from Mr. Bacon	1.5186
C/55 C.	1.5121
C/75 C.	1.5116
C/83 C.	1.5167
A No. 19	1.5163
R. M. S. 3505	1.5099
W. K. C. W. O.	1.5110

The results in Tables II and III require little comment; they show clearly that the admixture of small amounts of other drying oils lowers the refractive index.

TABLE II.

Sample.	Index of refraction at 25° C.
100 per cent. wood oil (mark) A.3.20.12	1.5147
95 per cent. wood oil, 5 per cent. soya bean oil	1.5122
95 per cent. wood oil, 5 per cent. linseed oil	1.5128
90 per cent. wood oil, 10 per cent. linseed oil	1.5114
100 per cent. soya bean oil	1.4751
100 per cent. linseed oil	1.4810

TABLE III.

Sample.	Index of refraction at 25° C.
100 per cent. wood oil (Bacon's sample)	1.5186
95 per cent. wood oil, 5 per cent. soya bean oil	1.5163
95 per cent. wood oil, 5 per cent. tallow oil	1.5161
100 per cent. tallow oil	1.4833

All indices of refraction were taken *without* the use of water circulation. All refractometric readings were made in the Advanced Physics Laboratory of Columbia University.

* The explanation of these high refractive indices will probably be found in the examination of the chief constituent of the oil, namely, the remarkable glyceride of oleomargaric acid, which is present in *none* of the other common drying oils.

[1] *Private communication.*

In conclusion, I beg to thank Mr. Bloch, chemist for the Standard Varnish Works, for his material aid, Dr. C. C. Trowbridge, of the Department of Physics of Columbia University, for his kind advice and Dr. Parker C. McIlhiney for his just criticism and his help.

LABORATORIES OF THE STANDARD VARNISH WORKS,
ELM PARK, N. Y.

THE REFRACTIVE INDEX OF BEESWAX.[1]

By L. FELDSTEIN.

Received Jan. 5, 1912.

Lewkowitsch, in "Chemical Technology and Analysis of Oils, Fats, and Waxes," recommends refractometric examination as a preliminary test in the examination of beeswax, giving as the limits between which pure beeswax should fall, 42.9°–45.6°; butyro-refractometer scale, calculated to 40° C. These figures were obtained from the work of Werder[2] and Berg,[3] who made the determinations at temperatures ranging between 70° and 84° C. and then calculated them to 40° C. Neither Werder nor Berg in their original articles give the figures actually observed nor explain how their calculations were made, but it is assumed that they added to the observed figures the correction 0.55° butyro for each degree centigrade between the observed figures and 40° C., the correction value 0.55° being generally used for all fats and oils when calculated to 40° C. In this laboratory an Abbe-Zeiss direct-reading refractometer is used, and for beeswax a correction of 0.00037 per degree centigrade was found necessary. This figure was obtained by taking the refractive index at 65°, 75°, and 85° C. and dividing the difference in the reading by the difference in degrees centigrade. This correction of 0.00037 per degree centigrade was found to be practically constant between these temperature limits not only for all pure beeswax examined, but also for those which, upon further examination, showed adulteration.

As beeswax is a solid at 40° C. and the refractive index is always read on the melted wax at some temperature above 63° C., it seems desirable to eliminate the use of the calculation to 40° C. and to set limits for the refractive index of pure beeswax at some temperature above the melting point. For this purpose a number of samples of known purity and origin, obtained from the Bureau of Entomology, United States Department of Agriculture, and some others purchased on the open market were examined. All of these have been analyzed by the drug laboratory of the Bureau of Chemistry. The readings were made at 65°, 75°, and 85° C., and the results are given in the following tables. Table I consists of the figures obtained on the samples of pure beeswax secured from the Bureau of Entomology. Table II shows the results on those samples obtained in the open market, many of them adulterated samples. In the column headed "Remarks" are placed conclusions as to the nature of the sample based on the chemical analysis:

[1] Contribution from the Contracts Laboratory, Bureau of Chemistry Washington, D. C.

[2] *Chem. Ztg.*, **22**, 59 (1898).

[3] *Ibid.*, **27**, 752 (1903).

TABLE I.—REFRACTIVE INDEX READINGS AT DIFFERENT TEMPERATURES ON BEESWAX SAMPLES OF KNOWN PURITY.

Contract laboratory No.	Refractive index. At 65° C.	At 75° C.	At 85° C.	Locality.
12616	1.4458	1.4424	1.4390	Not given
12617	1.4458	1.4425	1.4391	"
12618	1.4456	1.4420	1.4380	"
12619	1.4454	1.4418	1.4378	"
12620	1.4449	1.4414	1.4380	Mexico
12621	1.4453	1.4416	1.4377	North Carolina
12622	1.4460	1.4426	1.4388	Wisconsin
12623	1.4441	1.4403	1.4365	Cuba
12624	1.4449	1.4412	1.4375	Habana
12625	1.4448	1.4410	1.4374	Haiti
12626	1.4448	1.4414	1.4374	Southern States
12627	1.4458	1.4424	1.4387	Africa
12628	1.4456	1.4420	1.4384	New York
12629	1.4488	1.4451	1.4415	San Domingo
12656	1.4440	1.4402	1.4363	Not given
12657	1.4443	1.4406	1.4367	Wisconsin
12658	1.4460	1.4424	1.4388	Illinois
12659	1.4449	1.4413	1.4377	Texas
12660	1.4444	1.4405	1.4368	Iowa
12661	1.4450	1.4413	1.4378	Utah
12662	1.4458	1.4422	1.4384	Iowa
12663	1.4444	1.4405	1.4368	California
12664	1.4436	1.4398	1.4361	Hilo
12665	1.4434	1.4398	1.4361	"
12666	1.4435	1.4400	1.4362	"
12667	1.4447	1.4410	1.4375	Not given
12801	1.4470	1.4433	1.4395	Minnesota

TABLE II.—REFRACTIVE INDEX READINGS AT DIFFERENT TEMPERATURES ON COMMERCIAL SAMPLES.

Contract laboratory No.	Refractive index. At 65° C.	At 75° C.	At 85° C.	Remarks.
12630	1.4463	1.4425	1.4389	Pure wax
12631	1.4459	1.4425	1.4387	"
12632[1]	1.4379	1.4340	1.4302	Paraffin present
12633	1.4456	1.4421	1.4387	Pure wax
12634[1]	1.4380	1.4344	1.4307	Paraffin present
12635[1]	1.4379	1.4342	1.4302	Stearic acid and paraffin present
12636	....	1.4540	1.4505	Resin present
12637[1]	1.4375	1.4338	1.4301	Paraffin present
12638[1]	1.4350	1.4313	1.4275	"
12639	1.4448	1.4410	1.4372	Pure wax
12640	1.4454	1.4416	1.4380	"
12641[1]	1.4421	1.4384	1.4346	Paraffin present
12642[1]	1.4363	1.4323	1.4284	"
12643	1.4447	1.4410	1.4372	Pure wax
12644	1.4437	1.4400	1.4364	"
12645	1.4440	1.4402	1.4368	"
12646	1.4445	1.4410	1.4372	"
12647	1.4438	1.4401	1.4362	"
12648[1]	1.4421	1.4384	1.4348	Paraffin present
12649[1]	1.4335	1.4300	1.4260	Stearic acid and paraffin present
12650[1]	1.4342	1.4304	1.4268	Paraffin present
12651	1.4439	1.4402	1.4365	"
12652[1]	1.4345	1.4307	1.4269	"
12653	1.4445	1.4408	1.4372	Pure wax
12654[1]	1.4355	1.4318	1.4280	Paraffin present
12655	1.4441	1.4406	1.4369	Pure wax

Upon examining the tables it will be found that the refractive index at 75° C. for pure beeswax falls between 1.4398–1.4451. Table II shows that the refractive indices of all those samples bought in the open market, which on chemical analysis appeared to be pure, fell within the limits for pure beeswax (1.4398–1.4451), while of the adulterated samples only one fell within these limits. This sample was No. 12651, which has a refractive index of 1.4402, a figure very close to the lowest value obtained for pure beeswax. In this instance it is quite possible that the beeswax had a high refractive index and was adulterated with a small amount of paraffin

[1] Grossly adulterated samples.

One sample (No. 12636), showing a high refractive index of 1.4540, proved on chemical examination to have resin in it. It was not possible to obtain a clear reading of this wax at 65° C. Those samples which have a very low refractive index proved to be grossly adulterated with either paraffin or stearic acid or both. A temperature of 75° C. was selected because at this point all beeswaxes are liquid, a clear, sharp line can be obtained in the refractometer, and it is comparatively easy to make the reading.

It is seen that the determination of the refractive index of beeswaxes is of great help in detecting gross adulteration and will generally reveal small adulterations, samples containing only a small amount of foreign material generally giving figures outside the limits mentioned, namely, 1.4398–1.4451 at 75° C. The results obtained show also that it is both unnecessary and unwise to calculate the refractive index to the butyro scale at 40° C., for the following reasons: (1) It is unreasonable to report the refractive index of a wax at a temperature at which it is an opaque solid, when the actual reading is made on the melted wax. (2) The calculation consumes time. (3) A clear reading can be obtained at 75° C. and the figures obtained can be reported unchanged.

THE CHEMISTRY OF ANAESTHETICS, IV: CHLOROFORM

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Received December 13, 1911.

(Continued from June No.)

VIII. The Examination of Anaesthetic Chloroform.

4. THE DETECTION OF WATER IN CHLOROFORM.

Since pure chloroform is not hygroscopic in the ordinary sense, and 100 cc. dissolve but 0.152 cc. of water at 22°,[1] such chloroform is not likely to contain appreciable amounts of water. In the case of anaesthetic chloroform, 0.025–0.05 per cent. by volume of water is introduced by the alcohol; it may be said, therefore, that the maximum amount of water likely to be present in anaesthetic chloroform is approximately 0.2 per cent. by volume, although the usual amount is about 0.05 per cent., according to our experience. Tests for the presence of water in anaesthetic chloroform are generally not specified. Since, however, the presence of water facilitates oxidation, it is at least desirable that the amount present is not excessive; and occasions may arise which require anhydrous chloroform. The authors are able to present tests, by the application of which both of these conditions may be met.

A. Tests Based upon the Evolution of Gas.

(a) *The Test with Calcium Carbide.*—Vitali[2] found that calcium carbide serves for the detection of water in chloroform; and we have learned that it is both a convenient and generally suitable reagent for the presence of water, even in minute amounts, in chloroform of all grades. It is the test which we recommend for establishing the anhydrous nature of a chloroform desired in a water-free condition.

[1] Herz, *Ber.*, **31**, 2670.

[2] *Boll. chim. farm.*, **37**, 257; cf. Baskerville and Hamor, THIS JOURNAL, **3**, 311.

When pure chloroform containing an addition of 0.025 per cent. by volume of water is agitated with *anhydrous cupric sulphate*, no reaction indicative of the presence of water is had; whereas if 20 cc. of the same chloroform is gently boiled over 1 gram of calcium carbide, and the gas evolved is passed into an ammoniacal silver nitrate solution, a pronounced acetylene reaction is obtained. In fact, since 1 gram of water yields, at 0° and 760 mm., 580 cc. of acetylene, the merest traces of water may be detected in chloroform of all grades by boiling the sample under examination over clean crystals of calcium carbide, and passing the vapors evolved into ammoniacal silver nitrate solution.

(*b*) *The Action of Copper-Zinc Couple on Chloroform.*—Gladstone and Tribe[1] found that copper-zinc couple did not act on pure chloroform, but that in the presence of alcohol at +60° C., methane was evolved, together with a small amount of acetylene, and in the presence of water, methane was evolved even at +12° C. This reaction is not adaptable as a test for the presence of water.

(*c*) *The Action of Sodium on Chloroform.*—Sodium acts on chloroform containing water,[2] but in such a manner that it cannot be employed as a reagent for the presence of water in this case.

(*d*) *The Test with Anthraquinone and Sodium Amalgam.*—The authors have reported[3] that "hydroanthraquinone" serves for the detection of both water and alcohol in ethyl ether. When several mg. of anthraquinone and a small piece of 2 per cent. sodium amalgam are added to 20 cc. of anaesthetic chloroform containing 0.8 per cent. of absolute alcohol and 0.025–0.065 per cent. of water, an alcohol reaction alone is obtained; with anaesthetic chloroform containing 0.115 per cent. of water, a faint, but decided, water reaction is had, although this is somewhat masked by the alcohol reaction, the amalgam becoming colored green and red in places. The test is not recommended for the detection of water in chloroform containing alcohol.

B. Tests Dependent upon the Production of a Turbidity.

(*a*) *Tests wherein the Chloroform is Cooled to Low Temperatures.*—Behal and Francois[4] considered that the simplest test for the presence of water in chloroform was to bring some of the crystals of ice obtained by submitting chloroform to a temperature of —20° to —40° in contact with mercuric ammonium iodide, when red mercuric iodide resulted. Chloroform freed from water does not afford any crystals of ice when exposed to the low temperature, and therefore pure chloroform should comply with this qualitative test; but since the addition of 5 parts of 98 per cent. alcohol in 1,000 causes them to appear, the test cannot be used for determining whether or not anaesthetic chloroform contains a *permissible* amount of water. The French *Codex* requires that anaesthetic chloroform shall not become turbid on cooling to —10°. Chloroform of the grade official in France should readily comply with this requirement for the following reasons: Chloroform saturated with water at +20° becomes turbid white or grayish on sudden cooling to —20°, owing to the formation of dispersed ice; but in a water concentration below 0.05 per cent. by weight of water in chloroform, there is no turbidity, although, according to Ostwald,[1] the Tyndall effect is pronounced down to 0.02 per cent. water.

(*b*) *The Test with Paraffin Oil.*—According to Crismer,[2] the "liquid paraffin" of the German pharmacopoeia[3] mixes in all proportions with anhydrous chloroform, but if water is present the liquid becomes turbid.

In order to determine the delicacy of this test, a sample of anaesthetic chloroform containing 0.8 per cent. by volume of alcohol and 0.04 per cent. by volume of water was taken. When 10 cc. of this sample were agitated with an equal volume of paraffin oil (sp. gr. = 0.880), the oil dissolved to a clear solution, without any evidence of a turbidity. When the water content was increased to 0.065 per cent. by volume, the solution still remained clear and transparent; but when 0.09 per cent. of water was present, a faint yet decided turbidity resulted. When chloroform contains 0.118 per cent. of water, the reaction is very pronounced.

C. Tests Based on the Color Assumed by the Hydration of a Dehydrated Compound.

(*a*) *The Test with Anhydrous Cupric Sulphate.*—Since anhydrous cupric sulphate is a very satisfactory reagent for the presence of water in ethyl ether, the salt was tried in this connection. None of the commercial or anaesthetic chloroforms examined by us gave a response, when 20 cc. were shaken with 1 gram of anhydrous cupric sulphate during one hour; in fact, only a faint reaction was had with anaesthetic chloroform containing 0.115 per cent. of water, and a marked response was obtained only when the saturation point of the chloroform was reached.

D. Recommendations.

Pure chloroform and anhydrous anaesthetic chloroform should comply with test *A* (*a*); and anaesthetic chloroform should readily conform to test *B* (*b*), although it is highly expedient that the amount of water present be reduced to a trace, if not totally excluded, which could be accomplished by preserving anhydrous chloroform with anhydrous alcohol.

5. THE DETECTION AND ESTIMATION OF ALCOHOL IN CHLOROFORM.

The presence of ethyl alcohol in chloroform, in amounts varying from 0.25–1.00 per cent., has been almost universally recognized as necessary; in fact, all grades of chloroform on the market contain alcohol.

[1] *J. Chem. Soc.*, **28**, 508.

[2] Kern, *Chem. News*, **31**, 121. The reaction is in apparent accordance with this equation: $CHCl_3 + 3Na + H_2O = 2NaCl + NaOH + HCl + C + H$. With pure chloroform, however, sodium formate is obtained, and the variables of anaesthetic chloroform would render the use of sodium as a test of no value. The action of sodium on anaesthetic chloroform will be discussed more fully in Section 5.

[3] THIS JOURNAL, **3**, 310.

[4] *J. Pharm. Chim.*, **5**, 417 (1897). It is almost needless to state that none of the samples of chloroform examined by Behal and François complied with this test.

[1] *Z. Chem. Ind. Kolloide*, **6**, 183.

[2] *Ber.*, **17**, 649.

[3] B. p. = 215–240° under 6 mm. pressure.

Therefore, whenever it is desirable that chloroform intended for certain chemical work should be alcohol-free, it is necessary to resort to methods of purification which serve to eliminate alcohol; but in such cases it is always important that the purified chloroform be tested to prove the absence of alcohol, for which purpose sensitive qualitative tests are necessary. In the case of anaesthetic chloroform, the amount of alcohol present need not exceed the specified pharmacopoeial limits, and then, in general, qualitative tests are valueless in practice[1] and it is necessary to determine the amount present by a determination of the specific gravity or, preferably, by a quantitative estimation of the amount of alcohol. It should be mentioned here, however, that at the present time alcohol is seldom present in anaesthetic chloroform in excessive amounts.[2] Anaesthetic chloroforms on the American market generally contain 0.50–0.84 cc. of alcohol, calculated as absolute, per 100 cc., and only one sample examined by us contained as much as 0.97 cc. of absolute alcohol.[3]

With the object of finding just what tests and methods of estimation are suitable and reliable, all of the schemes for the detection and determination of alcohol in chloroform were studied, and where the method appeared worthy it was tried out. For convenience sake, these methods will be considered in classes.

A. Physical Methods.

(*a*) *The Determination of the Amount of Alcohol from the Density.*—It has been quite a general practice to infer the amount of alcohol present in any sample of chloroform from the specific gravity of the sample in question, and it is generally considered that this inference may be accomplished accurately; but as alcohol does not reduce the density in exact ratio to its amount, several investigators have found it necessary to determine the specific gravity of known mixtures of absolute alcohol and chloroform.[4]

Provided the past history of the sample is known, the density of anaesthetic chloroform is an indication of the amount of alcohol present, and therefore the percentage of alcohol may be approximately estimated therefrom; but we consider that after a determination of the specific gravity has been made, no conclusions as to the percentage of alcohol should be arrived until a quantitative estimation is carried out.

(*b*) *The Influence of Alcohol on the Boiling Point.* While alcohol may be readily identified in anaesthe chloroform by fractionation,[1] and may be partia eliminated by this means, the variables of such chlo form render the determination of its boiling po valueless as a criterion of purity.

B. Chemical Methods.

1. Tests Based on the Oxidation of Alcohol:—

(*a*) *The Chromic Acid Test.*—Several[2] have p posed that sulphuric acid and potassium dichroma be used as a reagent for the detection of alcohol chloroform. The test serves to prove the absence alcohol,[3] and is given in the pharmacopoeias of It and Spain.

Based on the oxidation of alcohol by chromic ac Nicloux[4] devised a method for the estimation of al hol in chloroform, according to which the small p portion of alcohol added is separated by shaki 5 cc. of the sample with 20 cc. of water; 5 cc. the alcoholic solution (containing not more than part in 500) are mixed in a test tube with 0.1–0.2 of a solution of potassium dichromate (19 g. per and then with pure sulphuric acid (sp. gr. 1.84), add cautiously. When sulphuric acid is added in sufficie quantity (4.5–6 cc.), the solution is decolorized; a the liquid is now gradually titrated with the dichroma solution, being shaken and gently heated after eve addition, until the color changes from greenish blue a permanent greenish color. This change, we m note, is most readily recognized in solutions contain less than 0.2 per cent. of alcohol. It is advisable make a second determination in which the amount dichromate used in the first experiment, less 0.1 is run in at once, the sulphuric acid added, and liquid is heated to boiling. The contents of the tu should remain greenish blue, while in another det mination in which 0.1 cc. more than the first read is added, the color should change to greenish yell The number of cc. consumed, divided by 1,000, gi the amount of absolute alcohol in cc. per cc. of soluti When the proportion of alcohol is less than 0.1 cent., the strength of the dichromate solution sho be doubled. Although Pozzi-Escot[5] found that order to obtain comparable results with the meth

[1] Cf. Dott, *Pharm. J.*, [3] **12**, 769.

[2] Much of the chloroform in America in 1875 was, however, contaminated with alcohol; for, according to the report of Meigs, it possessed a density of 1.45 (see Normandy-Noad's *Commercial Hand-book of Chemical Analysis*, **1875**, p. 122).

[3] The official chloroform of the *Pharmacopoeia of the United States* is specified as a liquid consisting of 99–99.4 per cent. by weight of absolute chloroform and 0.6–1 per cent. of alcohol.

[4] Remys (*Arch. Pharm.*, [3] **5**, 31), assuming that "pure" chloroform possesses a density of 1.500 at 15° C., stated that the presence of 1/3 per cent. of alcohol reduced the density by 0.002 and 0.5 per cent. by 0.008. Rump (*Am. Chemist*, **6**, 359) gave the same results. Besnou (see *U. S. Dispensatory*, 18th edition, p. 378; and Vremon in Stohmann and Kerl's *Technischen Chemie*, **2**, 646) determined the specific gravities at 4.5° C. of mixtures of the "purest commercial" chloroform with small quantities of alcohol. Schacht and Biltz (*Pharm. J.*, **1893**, 1005) obtained the following data:

	At 15° C.
"Pure" chloroform	1.5020
"Pure" chloroform with 0.25 per cent. alcohol	1.4977
"Pure" chloroform with 0.50 per cent. alcohol	1.4939
"Pure" chloroform with 1.00 per cent. alcohol	1.4854
"Pure" chloroform with 2.00 per cent. alcohol	1.4705

[1] On this point, see also Rump, *Am. Chemist*, **6**, 359; Behal and F çois, *J. Pharm. Chim.*, **5**, 417 (1897); Ryland, *Am. Chem. J.*, **22**, On the boiling points of alcohol and chloroform mixtures, see Thaye *Phys. Chem.*, **3**, 37; Wade and Finnemore, *J. Chem. Soc.*, **85**, 940.

[2] Cottell, *J. Pharm. Chim.*, [3] **13**, 359; Procter, *Am. J. Pharm.*, **1** 213; Fleischmann, *Polyt. Notizblatt*, **34**, 47; Gay, *J. Pharm. Chim.*, **4**, Rusconi, *Arch. farmacol. sper.*, **8**, 196. Cf., however, Lepage, *J. Ph Chim.*, **1860**, 93. Thresh (*Chem. News*, **38**, 251; see also, *Pharm. J.*, **11**, 319) proposed a method according to which the sample of chloro is agitated with an equal volume of water, the aqueous solution is dist with potassium dichromate and sulphuric acid, and the distillate is te for the presence of aldehyde by means of potassium or sodium hydro The presence of 0.5 per cent. of alcohol is thus made evident. The am of aldehyde produced may also be approximately determined colorim cally by means of the reagent of François (*Chem. News*, **76**, 7).

[3] See *Pharm. J.*, [3] **22**, 1041. It is, of course, very fallible, since m substances give the same reaction as alcohol.

[4] *Bull. soc. chim.*, [3] **35**, 330 (1906). The potassium dichro method of estimation is detailed in the French *Codex*.

[5] *Ann. chim. anal.*, **1902**, 11, 12.

of Nicloux for the estimation of alcohol in dilute solutions,[1] it was essential to maintain absolutely identical conditions, and that even then discordant results might be obtained in duplicate experiments; yet when the procedure above described is followed exactly, the method is very useful. There is but one important source of error, and that is that agitation of 5 cc. of chloroform containing alcohol with 20 cc. of water does not serve to deprive the chloroform of *all* the alcohol present; this can be accomplished, however, by repeatedly shaking the sample under examination with double its volume of water, which operation should be repeated at least ten times. The water-extracts may then be combined, and a suitable amount taken for analysis.

Behal and Francois[2] modified the method of Nicloux[3] by extracting the alcohol by agitation with sulphuric acid, diluting the acid solution with water, and then gently distilling; a portion of the distillate is boiled with sulphuric acid, and dichromate solution (16.97 g. per l.) is added until a green, but not greenish yellow, tint is reached. Each 2 cc. of the solution corresponds to 0.01 gram of absolute alcohol. This method gives concordant and quite accurate results under the conditions observed. If, however, the result obtained indicates a higher amount of alcohol than 2 cc. per 1,000, it is necessary to dilute the distillate with water, and then repeat the determination.

(*b*) *The Test with Alkaline Potassium Permanganate.*—Since pure chloroform will not reduce an alkaline solution of potassium permanganate, Yvon[4] recommended a reagent (potassium permanganate, 1 part; "alcoholic potash," 10 parts; water, 250 parts) which changed from a violet to a green color when mixed with "impure" chloroform.[5] Since, however, the change is caused by alcohol equally with more objectionable impurities, the test is of no value, except in examining pure chloroform,[6] and in this case barium hydroxide should be used in place of potassium hydroxide.[7]

An analogous test is that proposed by Jolles[8] for the detection of aldehyde, ethylene, etc., in chloroform. Jolles found that pure chloroform did not act on potassium manganate, whereas an addition of about 2 per cent. of alcohol or similar oxidizable matter quickly caused a reduction.[1]

(*c*) *The Molybdic Acid Test.*—Davy[2] found that a solution of molybdic acid in concentrated sulphuric acid served as a reagent for the detection of alcohol in chloroform; but since this test is only capable of detecting the presence of 1 part of alcohol in 1,000 parts of chloroform[3] and reducing substances in general give the reaction, it cannot be said to be of value.[4]

(*d*) *The Nitric Acid Test.*—Kossa[5] has found that nitric acid (50 per cent.) and ethyl alcohol (90 per cent.) give a decided color reaction;[6] but this behavior is not applicable as a test for the presence of alcohol in chloroform, since it is lacking in sensitiveness.

2. The Iodoform Test:—

Undoubtedly the most delicate test for the presence of alcohol in chloroform is that of Lieben, as modified by Hager. Usually it is directed that the sample under examination be agitated with 5 volumes of water, the liquid passed through a wet filter, and that the filtrate be then examined. We recommend the following procedure for the separation of alcohol from chloroform: 10 cc. of the chloroform under examination are shaken in a separatory funnel with 4 cc. of concentrated sulphuric acid, which combines with any alcohol; the extraction is again repeated with 4 cc. of sulphuric acid, and finally with 2 cc. The sulphuric acid solution (10 cc.) is now mixed with 40 cc. of water, and the diluted solution is gently distilled until the distillate amounts to about 20 cc. In this way the ethyl- sulphuric acid is decomposed into sulphuric acid and alcohol, and the iodoform test may now be applied to 10 cc. of the distillate. Add 6 drops of a 10 per cent. solution of potassium hydroxide, and warm the liquid to about 50° C. A solution of potassium iodide, saturated with free iodine, is next added drop by drop with agitation, until the liquid becomes permanently yellowish brown in color, when it is carefully decolorized with potassium hydroxide solution. If alcohol is present, iodoform is gradually deposited at the bottom of the tube in yellow crystals.[7]

This test is not peculiar to alcohol, being produced also by acetone, aldehyde, isopropyl alcohol, propyl and butyl alcohols and aldehydes, various ethers, etc.; but *pure* chloroform should give absolutely no response when the test is applied in the manner indicated.

3. Tests based on Solubility:—

(*a*) *Tests wherein Various Dyes are Employed.*—Regnault[8] stated that if chloroform contained a trace

[1] *Bull. soc. chim.*, [3] **17,** 424; *J. Pharm. Chim.*, [6] **5,** 424.

[2] *J. Pharm. Chim.*, [6] **5,** 417.

[3] *Bull. de la Soc. Therap.*, **3,** 860.

[4] *Mon. Sci.*, [3] **12,** 262 (1882); *J. Pharm. Chim.*, [5] **5,** 225.

[5] Yvon found that the rapidity of the change depends on the purity of the chloroform, and suggested that all chloroform which reduces the reagent within ten minutes should be considered incompletely purified or altered. Gay (*J. Pharm. Chim.*, **4,** 259) devised a method for estimating approximately the amount of alcohol in chloroform by means of Mohr's solution; this method is rapid, but the results obtainable are too indefinite.

[6] Dott, Clark and also Gilmour (*Pharm. J.*, [3] **12,** 769) discredited Yvon's proposed test as an indication of the purity of anaesthetic chloroform. Martindale (*Ibid.*, [3] **12,** 734) found that the British chloroform of 1882 would not stand Yvon's test, but considered that this failure was not due to the alcohol present; this was denied by Clark (*Ibid.*, 760), who, considering it necessary to add alcohol, stated that Yvon's test is worthless when such a procedure is followed. Preston (*Ibid.*, 981) believed that Yvon's test is a failure, since chloroform containing dangerous impurities cannot be differentiated from anaesthetic chloroform by its use alone. On this test, see also Portes, *Ibid.*, [3] **12,** 268; and Lotze, *Rep. anal. Chem.*, **1883,** 29.

[7] Cf. De Koninck, *Z. angew. Chem.*, **1889,** 4.

[8] *Chem. Ztg.*, **11,** 786.

[1] See Loevy and Jolles, *Chem. Ztg.*, **11,** 1394.

[2] *Chem. News*, **34,** 137; see also Boettger, *Z. Allg. Oest. Ap Ver.*, **1879,** 431.

[3] See Dott, *Ibid.*, 191. Dott pointed out that a determination of the density is a more delicate test for the presence of alcohol.

[4] Cf. Gladstone and Tribe, *J. Chem. Soc.*, **43,** 346.

[5] *Pharm. Centralh.*, **46,** 893.

[6] A white cloudy layer appears at the surface of contact after the alcohol is carefully poured on to an equal amount of the acid, and soon afterwards a green or bluish green ring is observed on the lower side of this; the green layer sinks gradually, effervescence occurs, and aldehyde "is formed."

[7] For details concerning the iodoform test, see Hager, *Z. anal. Chem.*, **9,** 492; *Pharm. J.*, [3] **1,** 683; *Pharm. Centralh.*, **1870,** 155. This test is capable of detecting 1 part of alcohol in 2000 of water.

[8] *J. Pharm. Chim.*, [4] **29,** 402.

of alcohol, it was colored purple on agitation with "Hofmann's violet," which is quite insoluble in pure chloroform; and also reported that chloroform should not dissolve or be colored by "aniline blue"[1] or fuchsine.[2] Stoedeler recommended fuchsine for the detection of alcohol in chloroform;[3] and Allen[4] attempted to apply rosaniline acetate in the estimation of alcohol. The *Nueva Farmacopea Mexicana*[5] gives the "aniline violet"[6] test. Behal and Francois[7] rejected the magenta test as too delicate, they having been unable to prepare chloroform which was not rapidly colored in contact with air by this reagent; it is indeed difficult to prepare chloroform which affords no coloration with rosaniline acetate, for example, and it is sufficient to require that pure chloroform shall give but a very slight coloration, if any, after continued agitation.

(*b*) *The Test with Potassium Hydroxide.*—Potassium hydroxide is quite insoluble in anhydrous chloroform, but dissolves sensibly in the presence of water or alcohol. Blachez[8] therefore proposed the following test for the presence of alcohol: Add to the sample a small piece of potassium hydroxide, and leave the mixture at rest for several minutes; decant the chloroform, shake with water, and add a solution of a copper salt to the aqueous extract; if a precipitate forms, it may be generally assumed that the chloroform contains alcohol.

A more reliable method, however, is to add to the chloroform under examination a small piece of fused potassium hydroxide and red litmus paper; if the latter assumes a blue color on being shaken with the chloroform, the presence of either water or alcohol is indicated.

To distinguish between water and alcohol, the sample may be agitated with ignited potassium carbonate, which treatment removes any water present; if the chloroform still possesses the power of dissolving potassium hydroxide, the presence of alcohol may be assumed. Pure chloroform should comply with this test.

(*c*) *The Test with Iodine.*—It was pointed out in 1869[9] that when chloroform is free from alcohol or ether, the color produced when iodine is dissolved in it is bright red; but when either alcohol or ether is present, the color of the solution is brown.[10] Siebold[11] proposed a method[1] for the detection and approximate estimation of alcohol in chloroform by the use of iodine, but it is not delicate.[2]

(*d*) Oudemanns[3] found that the proportion of alcohol contained in chloroform may be determined by means of cinchonine,[4] but the method is neither delicate nor practical.

4. *Miscellaneous Tests.*

The other tests which have been proposed for the detection of alcohol in chloroform are the iron dinitrosulphide test of Roussin,[5] the sulphuric acid test of Guthrie,[6] the test with sodium proposed by Hardy,[7] the potassium test of Mialhe,[8] the test depending upon the solution of the alcohol in water which originated with Soubeiran,[9] the albumen test of Kappeler,[10] and the almond oil test.[11] These tests are either not

[1] Regnault probably referred to rosaniline blue.

[2] *Mon. sci.*, [3] **12,** 262.

[3] The sample becomes colored red if alcohol is present, and the depth of the coloration varies with the proportion of alcohol.

[4] *Analyst,* **2,** 97. Chloroform containing alcohol still dissolves rosaniline acetate after treatment with calcium chloride; agitation with concentrated sulphuric acid eliminates alcohol and water, but the product retains so much acid it cannot be directly tested with fuchsine; the acid may be got rid of by means of potassium carbonate, but the chloroform retains sufficient alkali to prevent the coloration, and barium carbonate is more satisfactory; but when the dealcoholized chloroform is fractionated, these difficulties are not encountered.

[5] **1904,** p. 477.

[6] Methyl-aniline violet is undoubtedly referred to.

[7] *J. Pharm. Chim.*, **5,** 417 (1897).

[8] *Neues Jahrb. Pharm.*, August, 1869; *J. Pharm. Chim.*, [4] **9,** 289; *Z. anal. Chem.*, **8,** 472; *Russ. Z. Pharm.*, **8,** 582. See also Vogel, *N. Rep. Pharm.*, **18,** 306.

[9] *Pharm. Z. Russland*, March, 1869.

[10] In order to distinguish between alcohol and ether, a crystal of fuchsine was added to the chloroform; when a red solution ensued, the presence of alcohol was assumed.

[11] *Pharm. J.*, [3] **10,** 213.

[1] A small quantity of iodine is introduced into 10–15 cc. of the sample, which is then shaken until the solution has acquired a purple or purplish red color, but not opaque; the solution is decanted from the undissolved iodine, and is divided into two parts, which are placed in two separate test tubes of equal diameter. One is shaken with about four times its volume of water, and the other is kept for comparison. The water absorbs alcohol, and what settles down is a solution of iodine in chloroform, the color of which will be exactly the same as that of the other portion if the chloroform is "pure," but will be distinctly different if the sample contains alcohol.

[2] With 2 per cent. of alcohol or more, the difference is striking; with 1 per cent., it is distinct; and with 0.5 per cent., it is discernible; but 0.25 per cent. may only be definitely detected by resorting to distillation and then using the first portion of the distillate.

[3] *Ann.*, **166,** 1; *Z. anal. Chem.*, **11,** 409.

[4] 10 cc. of the sample are shaken with an excess of pure, dry cinchonine in a flask; the latter is kept for an hour at 17° C., with frequent agitation, and the liquid is then passed through a dry filter and 5 cc. of the filtrate are evaporated to dryness in a small beaker. The amount of residual alkaloid is then determined. Pure chloroform yields 21 mg., while chloroform containing 1 per cent. of alcohol yields 67 mg.

[5] *J. Pharm. Chim.*, [3] **34,** 206; see also *Am. Apoth. Ztg.*, **20,** 32. Pure chloroform shaken up with iron dinitrosulphide remains colorless; but if it contains alcohol, ether or wood spirit, it acquires a dark color. Kappeler, referring to this test in his *Anaesthetica*, states that the reaction is also caused by aldehyde and amyl alcohol. According to Lepage (*J. Pharm. Chim.*, **1860,** 93), the test of Roussin will detect one-thousandth part of alcohol. On this test, see also *Pharm. Centr.*, **1899,** 199.

[6] *Am. J. Sci.*, [1] **22,** 105. In 1832, Guthrie stated that sulphuric acid affords "a fine test of the presence of alcohol; if alcohol be present, so soon as the chloric ether is all over, the acid acts upon the alcohol which it has detained, and generates sulphuric ether, which is instantly indicated by its peculiar flavor; if no alcohol be present, no sulphuric ether will be produced."

[7] *Pharm. J.*, [2] **4,** 62; *Chem. News*, **5,** 286. Hardy considered that when a small piece of sodium remains unattacked in chloroform, the latter is pure. When, however, the sample contains alcohol or other substances susceptible of alteration, a disengagement of gas occurs. Traub (*Pharm. Centralh.*, **33,** 245) stated that there should be no deposit of *colored* sodium chloride; he confused alcohol with aldehyde.

[8] *J. Chim. Med.*, [3] **4,** 279.

[9] See Kessler, *J. Pharm. Chim.*, [3] **13,** 161. Mialhe (*Pharm. J.*, **7,** 345) proposed that a small quantity of the chloroform be dropped on some distilled water, when, if the sample is pure, it remains transparent; if, however, it contains alcohol, the globules acquire a milky opacity. With 1/300th part of absolute alcohol, the opalescence is marked (Mialhe).

Letheby (Normandy-Noad's *Commercial Hand-book of Chemical Analysis*, **1875,** p. 121) adopted a similar test, but recommended that the amount of alcohol dissolved be determined by the diminution in bulk of the chloroform after shaking with water. The proportion of alcohol in anaesthetic chloroform can be determined only with tolerable accuracy by means of this method when the quantity present exceeds 1 per cent. "On the Estimation of Alcohol by Glycerine," see Hager, *Z. anal. Chem.*, **1889,** 375; and "On the Solubility of Chloroform in Water," cf. Chancel and Parmentier, *Compt. rend.*, **106,** 577.

[10] *Anaesthetica, Loc. cit.* Kappeler stated that alcohol may be recognized in chloroform by the coagulation which occurs in the white of egg when a few drops of the sample are added.

[11] This test was also devised by Soubeiran. Lepage found that it will not serve to detect a smaller quantity of alcohol than 5–6 per cent. (*Pharm. J.*, **11,** 213). Hager (*Kommentar*, **1865,** p. 439) gave the limit of delicacy as 4–5 per cent. of alcohol.

characteristic of the presence of alcohol alone or are wanting in necessary delicacy, and all are unsatisfactory.

C. Recommendations.

(*a*) Pure chloroform should possess a correct specific gravity and boiling point, and should give no response when tests 1 (*a*), 1 (*b*), 2 and 3 (*b*) are applied.

(*b*) In the case of anaesthetic and commercial chloroform, a determination of the density should first be made, and then a quantitative estimation of the amount of alcohol present by the method of Nicloux as elaborated by the authors [1 (*a*), *supra*]. Anaesthetic chloroform should not contain over 1 cc. of alcohol, calculated as absolute, in 100.

6. THE DETECTION OF ACETONE IN CHLOROFORM.

Since chloroform is now largely manufactured from acetone, this is a probable contaminant of anaesthetic and commercial chloroform, and it is sometimes necessary to test for it[1]—a difficult procedure if present in likely amounts.

Pure chloroform complying with the iodoform test as described is assuredly free from acetone; but the detection of acetone in anaesthetic and commercial chloroform presents greater difficulties. The tests wherein advantage is taken of the solubility of mercuric oxide in acetone (Reynolds) and of the solubility of mercuric sulphate in acetone (Denigès) are not applicable in this case. This is principally due to the fact that chloroform containing any likely amounts of acetone will not part with sufficient of the compound to afford a response; in fact, we obtained negative results with chloroform containing 1 part of acetone in 500 of anaesthetic chloroform. The tests with silver nitrate solution,[2] potassium hydroxide and hydrated oxide of silver[3] are not decisive, being generally indicative of the presence of acetaldehyde, and for this reason alone cannot be considered in this connection.

We have found the following test satisfactory in the absence of all but comparative traces of acetaldehyde:[4] 10 cc. of the sample of anaesthetic or commercial chloroform are agitated with 5 drops of a 0.5 per cent. sodium nitroprusside solution and 2 cc. of ammonium hydroxide (sp. gr. 0.925), and then allowed to stand several minutes. Chloroform containing up to 1 per cent. of alcohol may impart a yellowish brown color to the supernatant liquid on agitation, but when acetone is present there results an amethystine color. On adding solid ammonium sulphate to the mixture, then shaking and allowing to stand several minutes, in the case of acetone-free anaesthetic chloroform a yellow color results, while in the presence of acetone the amethyst color disappears, but reappears on standing 5 minutes. This test must be conducted in the cold.[1] It is also subject to the limitations of solubility referred to above, but is the only convenient test to our knowledge and anaesthetic chloroform should give a negative reaction when it is applied. In the presence of 1 part of acetone in 500 of anaesthetic chloroform, the amethyst color is marked; when the proportion is 1 : 1,000, the coloration is not distinct until the mixture of chloroform with ammonium hydroxide and sodium nitroprusside has been saturated with ammonium sulphate, shaken and then allowed to stand five minutes, when a decided amethystine color is observed. The coloration is, in all cases, rendered apparent by comparing with a blank.

We recommend that the above test be applied to the suspected chloroform direct, and then to the first 10 per cent. distillate and to the 10 per cent. residuum, obtained by the fractionation of 100 cc. of the sample; and anaesthetic chloroform should give a negative result in all cases.

7. THE DETECTION OF METHYL ALCOHOL AND OTHER METHYL COMPOUNDS IN CHLOROFORM.

Reference has been made to the manufacture of chloroform from "methylated spirit."[2] When such chloroform is properly purified, it is identical with that prepared from alcohol or acetone; but it is only in anaesthetic or commercial chloroform prepared from "methylated spirit" that one may reasonably suspect the presence of methyl alcohol. Various tests have been proposed in the past for the detection of this then probable contaminant;[3] but chloroforms now on the market are, so far as we have been able to ascertain, free from methyl alcohol, formaldehyde and formic acid, and, at all events, it is unnecessary to test for the presence of these substances in anaesthetic and commercial chloroforms at present on the American market.

8. THE DETECTION OF ETHYL ETHER IN CHLOROFORM.

From 1865–1875, ethyl ether was regarded as one of the general contaminants of anaesthetic chloroform and various tests were devised for its detection.[4] It

[1] Scholvien (*Pharm. Ztg.*, **32**, 686) pointed out that owing to the fact that chloroform was then (1888) prepared to a considerable extent from acetone, this substance is likely to occur as an impurity, the boiling points of the two bodies only differing by 5° C. Gerrard (*Pharm. J.*, [3] **23**, 231) found that on distilling 200 cc. of chloroform the last 2 or 3 cc. of residue contained traces of acetone bodies.

[2] See Gay, *J. Pharm. Chim.*, **4**, 259.

[3] See *The Detection of Aldehyde in Chloroform, Section 9.*

[4] The presence of 2 parts of acetaldehyde in 1,000 gives an intense reaction; when, however, the proportion becomes greater than 1 : 3300, acetaldehyde no longer interferes.

[1] Cf. Rothera's test for the presence of acetone in urine (*J. Physiol.*, **37**, 491).

[2] See III, **2**, in this paper.

[3] Ulex (*Arch. Pharm.*, [3] **5**, 523) stated that methyl alcohol may be detected in chloroform by means of sulphuric acid; but this is correct only when furfural is also present. Kappeler (*Loc. cit*) reported that chloroform containing methyl compounds forms a black oily layer when treated with zinc chloride; and Langbeck stated that silver nitrate may be used for distinguishing between the so-called methylated chloroform and that from alcohol, a precipitate of silver oxide being formed when "methyl" is present. Dott (*Pharm. J.*, [3] **9**, 524) showed that the test of Langbeck is worthless for the purpose claimed.

According to Normandy and Noad (*Commercial Hand-book of Chemical Analysis*, **1875**. p. 123), one of the best indications of the presence of methyl compounds is the effect which they produce upon the animal system!

The presence of methyl alcohol in chloroform may be determined by fractionation. 0.42 gram of methyl alcohol to 99.58 gram of chloroform forms a mixture which is said to begin to boil at 54.43° C.

[4] It was stated, for example, that any considerable admixture of ethyl ether with chloroform would be indicated by the inflammability and diminished density of the liquid. On the specific gravities of chloroform-ether mixtures, see Katz, *Apoth. Ztg.*, **17**, 514. Rosenthaler (*Arch. Pharm.*, **244**, 24) found that when chloroform and ethyl ether are mixed, under varying conditions, a notable rise of temperature invariably ensues.

Rabourdin (*Compt. rend.*, **31**, 786) reported that ether may be detected in chloroform by the addition of a trace of iodine—a test of absolutely no value.

Ether may be detected in anaesthetic chloroform by fractionation of the sample; this is the only suitable method (cf. *Farmacopea Italiana*, fourth edition, p. 1357).

is unnecessary to look for the presence of such an improbable impurity at the present time.

9. THE DETECTION OF ACETALDEHYDE IN CHLOROFORM.

Chloroform, whether made from alcohol or acetone, should be, and is, so far as we have been able to ascertain, free from appreciable amounts of acetaldehyde,[1] although in the past such contamination was quite general, owing to the use of impure alcohol, to imperfections in purification, and to careless storage. The alcohol present in anaesthetic chloroform is generally 95 per cent. rectified spirit, which should not contain over 1 part of acetaldehyde by volume in 10,000. Assuming the presence of this amount of aldehyde, and an addition of 1 per cent. of such alcohol to properly purified chloroform, it will be apparent that the anaesthetic chloroform manufactured in this way will contain a negligible amount of acetaldehyde. Since acetaldehyde is, however, the primary product of the oxidation of anaesthetic chloroform, delicate characteristic tests for its presence are necessary; and by the application of these it may be determined whether chloroform has been purified by means of a method serving to eliminate any acetaldehyde occurring in the crude product and whether the sample under examination has been stored in such a way as to prevent, at least for ordinary periods of time, oxidation of the alcohol present.

A. There have been a few tests proposed for the detection of acetaldehyde in chloroform. Of these, the silver nitrate[2] and "hydrate of silver oxide"[3] tests are not decisive; the test of Rusconi[4] is, among other things, lacking in necessary delicacy, while the test with potassium hydroxide,[5] the most satisfactory of the recommended tests, is not altogether characteristic of the presence of acetaldehyde, and there are, in addition, certain sources of error.[1]

Pure chloroform complying with the iodoform and chromic acid tests is certainly free from acetaldehyde; but the definite recognition of small amounts of this substance in anaesthetic chloroform presents greater difficulties.

We have found that when acetaldehyde is present in anaesthetic or commercial chloroform in appreciable amounts, it may be readily detected by agitating 5 cc. of the sample with an equal volume of the reagent of Francois (22 cc. sulphurous acid, 30 cc. 1 : 1,000 rosaniline acetate solution, and 3 cc. sulphuric acid), which also shows the presence of those very unusual contaminants, furfural and chloral.[2] The presence of 3 parts of acetaldehyde by volume in 10,000 of chloroform may thus be readily made evident, and even smaller amounts may be detected by fractionation.

When anaesthetic chloroform containing 6 parts of acetaldehyde in 10,000 is agitated with an equal volume of water, the water extract fails to respond with Francois' reagent; therefore the test should always be applied to the sample direct, as given above, and no coloration should result even after 15 minutes in the case of anaesthetic chloroform. This method may, obviously, be made *approximately* quantitative, since the amount of aldehyde may be determined colorimetrically by comparison with standards, just as in the case of ethyl ether.[3]

Confirmation may be had of the presence of aldehyde by applying the test with 1 : 10 metaphenylenediamine hydrochloride solution. 10 cc. of the sample should afford no coloration, even after one hour's standing, after being thoroughly agitated with the test solution.

B. The Deportment of Chloroform with Nessler's Reagent.—The *Pharmacopoea Nederlandica*[4] requires that 5 cc. of *chloroform ad narcosin* shall give no reaction in 12 hours on shaking it with solid potassium hydroxide. Stengel (*Z. Oester. Apoth. Ver.*, **46,** 279) claimed that no chloroform of the official specific gravity 1.485–1.490 will meet the requirements of the potassium hydroxide test of the Austrian pharmacopoeia. In Belgium it is required that chloroform shall impart no coloration to an equal volume of sodium hydroxide solution; potassium hydroxide is specified in Chili, Spain, and Mexico; and potassium hydroxide solution in Switzerland and France.

In the sixth revision of the *Pharmacopoeia of the United States* (1882) it was required that when a portion of chloroform was digested, warm, with a solution of potassium hydroxide, the latter should not become "dark colored."

It is true that pure chloroform is not visibly altered when heated with a solution of potassium hydroxide, although it is slowly acted on with formation of formate and chloride of potassium. In alcoholic solution this reaction occurs rapidly (see, in this connection, Desgrez, *Compt. rend.*, **125,** 780; Thiele and Dent, *Ann.*, **302,** 273); formic acid is produced by the secondary reaction of carbon monoxide on the alkali. The test with potassium hydroxide is not characteristic of the presence of acetaldehyde, however, being also indicative of contamination with acetone and extractive matter. A more decisive test is therefore necessary.

[1] Of the many samples of anaesthetic and commercial chloroform examined by the authors, only two contained excessive amounts of acetaldehyde. One of these, an unopened tin six years old, contained approximately 1 part of acetaldehyde in 3300; while the other, an unopened tin of chloroform manufactured in 1863, contained 1 part in 2000. Both of these samples also contained acetic acid, but the chloroform itself was unaltered. These findings support most convincingly the views already expressed as to the role of alcohol in preservation.

[2] Gay (*J. Pharm. Chim.*, [6] **4,** 259) proposed that the sample be shaken with an equal volume of 10 per cent. silver nitrate solution; a white precipitate on standing indicates the presence of hydrochloric acid, and a black precipitate on boiling that of aldehyde, *formic acid*, or *acetone*. See also Scholvien, *Pharm. Ztg.*, **32,** 686; Behal and François, *J. Pharm. Chim.*, [6] **5,** 417.

[3] This test, based on the reducing action of aldehyde on the "hydrated oxide" of silver, is given in the pharmacopoeias of Italy and Mexico.

[4] Rusconi (*Arch. farmacol. sper.*, **8,** 196) found that 0.1 per cent. of aldehyde may be detected in chloroform by means of sodium nitroprusside and $(CH_3)_2NH$, the test being made on the distillate.

[5] Letheby (*Loc. cit.*) pointed out that aldehyde may be occasionally met with in chloroform. He considered it questionable if it occasions any injurious influence when it is inhaled with the chloroform, but indicated the irritating action of acetic acid. He recommended the "hydrated oxide of silver" and "liquor potassae" tests. Regnault (*J. Pharm. Chim.*, [4] **29,** 402; see also *Mon. Sci.*, [3] **12,** 262) stated that aldehyde may be detected by many of the tests for ethyl alcohol, and also by warming with potassium hydroxide, when its presence is indicated by a darkening in color. Scholvien (*Pharm. Ztg.*, **32,** 686) found that a sample of chloroform, which, as regarded its density, boiling point, and reaction with both silver nitrate and sulphuric acid, satisfied the tests prescribed by the German Pharmacopoeia, possessed an odor of aldehyde. A piece of potassium hydroxide placed in the chloroform assumed a brown color, the chloroform itself becoming yellow in color. After treating the sample with alcoholic ammonia and gently distilling off the chloroform, the residue gave the characteristic odor of aldehyde-ammonia and a reaction with Schiff's reagent. Behal and François (*Loc. cit.*) stated that pure anaesthetic chloroform should not be colored by boiling with solid potassium hydroxide.

The Italian, Dutch and Austrian pharmacopoeias give this test for the presence of aldehyde. The chloroform should give no brown colora-

[1] For example, the potassium hydroxide used must contain over 80 per cent. KOH and *no water*, otherwise anaesthetic chloroform containing no aldehyde may give the coloration, owing to the oxidation of the alcohol in the chloroform. See Stengel, *Z. Allg. Oester. Apoth.-Ver.*, **46,** 279.

[2] "On the Detection of Traces of Chloral in Chloroform," see Jona, *Giorn. Farm. Chim.*, **61,** 57.

[3] See Baskerville and Hamor, THIS JOURNAL, **3,** 393, wherein the procedure of François (*Chem. News*, **76,** 7) is discussed.

[4] **1905,** p. 90.

tion when shaken with 5 cc. of water and 3 drops of Nessler's reagent—a comparatively stringent requirement,[1] for, while pure chloroform should, of course, give an absolute non-response with Nessler's reagent, since it is necessary to add alcohol for preservation, the test cannot be required wherein the reagent is used direct without dilution or other modification.

In order to determine the applicability of Nessler's reagent as a test for the presence of acetaldehyde in anaesthetic chloroform, the following experiments were performed, using 5 cc. of each sample and 5 cc. of Nessler's reagent U. S. P.:—

Sample and conditions.	Results.
1. Salicylid-chloroform, containing no detectable impurities; 0.25 per cent. pure ethyl alcohol.	Reagent assumed a faint opalescence after the mixture had been shaken and then allowed to stand 5 minutes.
2. Anaesthetic chloroform prepared from carbon tetrachloride and of full U. S. P. quality; 0.7 per cent. alcohol.	After 5 minutes, a turbidity was observed, but no coloration or precipitate.
3. A sample of anaesthetic chloroform prepared from acetone and complying in full with the requirements of the U. S. P.	Reagent assumed an orange opalescence after shaking and allowing to stand 5 minutes: after 10 minutes, the reagent became red colored.
4. An old sample of anaesthetic chloroform (48 years), which gave a marked reaction with François' reagent.	Reagent darkened immediately. After 5 minutes it possessed a dirty yellow color and a black precipitate was observed.
5. "Purified chloroform," of full U. S. P. grade; 0.9 cc. absolute alcohol in 100 cc.	After 5 minutes, the reagent possessed an opalescent orange color; it appeared turbid, but no precipitate settled out.
6. "Chloroform pure," of U. S. P. grade, and in addition conforming with the formalin-sulphuric acid test; 0.56 cc. absolute alcohol in 100 cc.	As in No. 5.
7. Anaesthetic chloroform prepared from chloral, and conforming with all requirements of the U. S. P. but the sulphuric acid test; 0.30 cc. absolute alcohol in 100 cc.	As in No. 5.
8. Anaesthetic chloroform conforming with all the requirements of the German Pharmacopoeia.	Red color at once; after 5 minutes, it became darker in color than No. 5.
9. Pure chloroform containing 1 part of acetaldehyde in 555.	Reagent assumed a brick-red color at once, but became black after several seconds; a heavy black precipitate after 5 minutes.
10. Pure chloroform containing an addition of 2 parts of acetaldehyde in 11,000.	Red color at once; a heavy brick-red precipitate after 5 minutes.
11. Ten cc. of pure chloroform containing an addition of 2 parts of acetaldehyde in 11,000; 10 cc. of water, and 5 drops of Nessler's reagent U. S. P.	Opalescent yellow color at once. After 5 minutes, the reagent possessed an opalescent orange-yellow color (turbid).
12. Ten cc. of No. 5; 10 cc. of water; and 5 drops of Nessler's reagent U. S. P.	No color at once, but a very faint yellow color after 5 minutes; the reagent was slightly turbid after agitation for 1 minute. The difference from the preceding was most marked.

From these general experiments, supplemented by tests made on various other anaesthetic chloroforms, it was concluded that the test with Nessler's reagent is more delicate in this case than that with the reagent of Francois; and that while *pure* anaesthetic chloroform should behave as in Experiment 1, in our opinion it is sufficient to require that anaesthetic chloroform should comply with the following test: When 10 cc. of the sample are agitated with 10 cc. of water and 5 drops of Nessler's reagent U. S. P., and the mixture is then allowed to stand 5 minutes, there should result no precipitate and the reagent should assume no coloration, although it may become opalescent or slightly turbid.

(To be concluded in the August No.)

[1] Cf. Weigel, *Pharm. Centralh.*, **47**, 400.

LABORATORY STUDIES OF RENNIN.[1]

I. A Study of the Properties of this Important Ferment, when Prepared by Different Methods. II. The Acceleration of the Action of Rennin by Phosphoric Acid. III. The Variation in the Length of Time Required to Curdle Different Specimens of Milk.

By A. Zimmermann.

Received January 17, 1912.

I. KINDS OF RENNIN.

Rennin Precipitated by Sodium Sulphate.—The rennets are digested to complete solution at 110° F. After separation of the fatty matter and clarification of the solution, this is precipitated by adding 3 volumes of a saturated solution of sodium sulphate, at 104° F.; the precipitate is collected, pressed and then dried at a temperature not exceeding 110° F. The yield is greater than that obtained by sodium chloride, the bulk being made up by albumose bodies. This makes it of a lower strength, ranging from 1 : 30,000 to 1 : 40,000 in 12 minutes.

Rennin Precipitated by Sodium Chloride.—The clarified solution of the rennets is saturated with sodium chloride at 104° F. The rennin is collected, pressed, then dried at a temperature not exceeding 110° F. The yield is much smaller than with sodium sulphate, giving a rennin of a much higher strength, from 1 : 150,000 to 1 : 200,000 in 12 minutes.

Rennin in Scales (Granular Rennin).—Prepared by scaling the clarified solution of the whole rennets at a temperature not exceeding 110° F. When perfectly dry, the scales are forced through a 16-mesh sieve. The strength of this rennin is from 1 : 30,000 to 1 : 40,000 in 12 minutes.

Commercial Rennin.—There are two different forms of rennin upon the market: (1) Rennin in powder form, prepared from the sodium chloride product, powdered and diluted with sugar of milk, testing 1 : 30,000 to 1 : 40,000 within 12 minutes. (2) Granular rennin, prepared from the scales, which also tests 1 : 30,000 to 1 : 40,000 within 12 minutes.

Difference between Precipitated and Scales Rennin.—The precipitated rennins are diluted with more or less albumose substance. They are acid in reaction, as they carry the greater part of the acid from the solution during the precipitation. The scaled rennin contains the soluble products, peptone and albumose

[1] Presented at A. C. S. meeting at Washington, D. C., December, 1911

substances, formed during the process of digestion of the rennets by aid of hydrochloric acid, which it also retains and which gives to it its acid reaction.

The rennin by sodium sulphate is no longer manufactured for use in the pharmaceutical preparations, the most important of these being the Essence of Pepsin, which is much used as a vehicle for bromides; the presence of sulphates would make it incompatible with strontium bromide. The complete separation of the sulphuric acid from rennin is not easily accomplished: by the use of calcium chloride, the reaction requires several days, during which time the rennin loses its activity; with barium chloride, there is formed a nearly colloidal barium sulphate, extremely difficult of separation.

The sodium chloride product is not so permanent as the granular rennin and the sodium sulphate product in a glycerine-water solution in the form of glycerol, which is a most excellent solvent for making permanent solutions of this class of substances.

The following tests made with a glycerol containing both rennin and pepsin, upon milk kept refrigerated for 17 to 18 hours after the milking, shows the permanency of the different forms of rennin, each giving a strength of 1 : 2500 in the time indicated:

RENNIN AND PEPSIN GLYCEROL.

Kind of rennin.	NaCl pptd.		Na_2SO_4 pptd.		Granular.	
No. of milk.....	1	2	1	2	1	2
When prepared...	12 min.	12 min.	12 min.	12 min.	12 min.	12 min.
After 1 mo.....	30 "	25 "	12 "	12 "	12 "	12 "
After 2 mo.....	2.5 hrs.	2 hrs.	12 "	12 "	12 "	12 "
After 12 mo.....	3.5 "	3.25 hrs.	12 "	12 "	12 "	12 "
After 15 mo.....			12 "	12 "	12 "	12 "

The permanency of the rennin in solution seemed to be dependent upon phosphoric acid. This is contained in the rennets probably as a calcium salt, and during the digestion of these, for the preparation of rennin, the phosphoric acid is liberated by the hydrochloric acid used in the process. The granular scale and sodium sulphate product react for phosphoric acid, and in this they differ from the sodium chloride product, which appears to contain but very small quantities or none.

II. ACTION OF PHOSPHORIC ACID.

The addition of phosphoric acid in the proportion of 0.075 per cent. to milk, from individual cows or that mixed from the herd, has the effect of increasing the activity of the rennin very much. This applies to milk from 4 to 8 hours after the milking; as the milk gets older the rennin acts more rapidly, and with milk 2 days old preserved by refrigeration, the curd is formed within a few minutes without the need of any accelerant. The curd formed in milk from 4 to 8 hours old forms very gradually after the action of the rennin sets in and, when complete, is not nearly so firm as that formed in the presence of the phosphoric acid, which reduces the time of action to between $^1/_{10}$ and $^1/_{20}$.

Lactic, hydrochloric and oxalic acids also have an accelerating action upon rennin, but less than phosphoric acid. Lactic acid possesses about $^1/_5$, and the other acids about $^1/_{10}$ the activity of phosphoric acid. Lactic acid forms a firmer curd than hydrochloric or oxalic acids, but not so perfect and firm a curd as is formed by the phosphoric acid:

COMPARATIVE ACTION OF RENNIN (R.) AND RENNIN ACCELERATED BY PHOSPHORIC ACID (R. P.).

Milk. Specimen.	4–5 hrs. old.		17–18 hrs. old.[1]		40–42 hrs. old.[1]	
	R. Min.	R. P. Min.	R. Min.	R. P. Min.	R. Min.	R. P. Min.
1.....	60	1.75	9.5	1	4.0	0
2.....	35	1.5	3.5	1	3.0	0
3.....	62	2.0	7.0	1	2.5	0
4.....	40	1.5	8.0	1	2.0	0
5.....	42	1.75	9.0	1	3.0	0
6.....	63	2.0	5.0	1	1.5	0

The glycerol solution, 12 months old, prepared with sodium chloride precipitated rennin, which requires 3 to 3.5 hours to curdle 18-hour milk, curdles this same milk in one minute when accelerated by phosphoric acid.

III. VARIABILITY OF MILKS.

The length of time required to curd by the same specimen of rennin seems to be influenced by the length of time the milk is kept after the milking, as already noted under "Action of Phosphoric Acid." There is a slight difference in the degree of acidity of the milk, that which curds the quickest being slightly more acid. Milk which curds very quickly with rennin can be modified to require a greater length of time to curd, by varying its degree of acidity by addition of an alkali. This is shown in the following table:

Milk. Cc.	*N* NaOH. Cc.	Curd formed in min.
75	0.0	0.5
75	0.6	0.5
75	1.2	13.0
75	1.5	None in 3 hrs.

Other investigators, Smeliansky[2] and Werncken,[3] have noted the effect of acids (other than phosphoric) and alkalies upon the rennin coagulation of cows' milk, and these same investigators, with Van Dam[4] and Gerber,[5] have observed the influence of many other substances in this same direction.

The tendency of the milk to curd more quickly the longer it is kept after milking would appear to be of bacterial origin; but if this be the cause, how can we explain why a mixture of rennin and milk kept at 104° F. for several hours does not curd, while if the milk is kept at that temperature for several hours the addition of the same rennin causes very quick curdling? In the latter case the influence of bacterial growth is suggested, and in the first case we also have all the conditions to favor bacterial growth and hasten the curd forming, but such action is not perceptible.

Fuld and Wohlgemuth[6] have found that cows' milk is more easily curdled after it has been frozen. According to Van Dam,[7] when milk is heated the acidity increases. My observations in this direction have been with milk 18 to 20 hours after milking; when heated for $2^1/_2$ hours at a temperature of 104° F., the

[1] Refrigerated.
[2] *Milchwirtsch. Zentr.*, **4**, 379–381; *Arch. Hyg.*, **59**, 187–215.
[3] *Z. Biol.*, **52**, 47–77.
[4] *Z. physiol. Chem.*, **58**, 295–330.
[5] *Compt. rend.*, **66**, 552; **68**, 201–207; **145**, 577; **147**, 1320.
[6] *Biochem. Z.*, **5**, 110–42.
[7] *Milchwirtsch.*, **5**, 154–155.

acidity was raised from 30 to 40 per cent. in different specimens. With milk 2 hours after milking, kept at 104° F. for 2½ hours, there was no change in the acidity.

The results of these investigations would indicate that acidity to within a limited degree influences the more rapid curdling of the milk by the rennin, but whether the increased acidity is directly of bacterial origin or due to a change in the acidity of the phosphates, will have to be proved by further investigation.

Standardized Rennin to Control Milk Used for Testing the Activity of Rennin.—To control the variability of milk for the assay of rennin it was found necessary to prepare a standard rennin to show whether the milk was fast or slow. This rennin was standardized by testing its action upon not less than 12 different specimens of milk, as daily supplied from a reliable source, and the average taken. Thus, if the rennin is standardized to 1 : 30,000 in 8 minutes, its use as a control with the rennin to be assayed readily shows whether the milk is fast or slow, and allowance is made accordingly. The rennin should be added to the milk as soon as it has the temperature of 104° F., for a longer time before the rennin is added makes it curd more rapidly.

Permanency of Rennin Solutions.—Aqueous solutions of rennin of a density 1.010, containing 0.20 per cent. by volume hydrochloric acid, lost 30 per cent. of their activity in one day at a temperature of 70° F. More concentrated solutions of a density 1.090 per cent., containing 1.30 per cent by volume hydrochloric acid, were more permanent. Elevation of temperature causes more rapid destruction. The denser the solution, the slower the destruction at an elevated temperature.

Essence of Pepsin.—The results here obtained would suggest the use of the granular scaled rennin and of phosphoric acid in place of lactic acid in the preparation of essence of pepsin. Investigations concerning the making of a permanent rennin preparation are now under way.

BROOKLYN, N. Y.

MICRO-CHEMICAL TESTS FOR THE IDENTIFICATION OF SOME OF THE ALKALOIDS.

By EARL B. PUTT.

Received January 29, 1912.

Though the use of certain precipitants for detecting alkaloids has been quite general for a long time, the characteristics of the precipitates so produced do not seem to have received the study which they deserve.

Most schemes of analysis employ these general precipitants to detect the presence of alkaloids and then rely upon various color tests to identify any particular alkaloid, without subjecting the first precipitate to any further examination. If the color tests which are, at present, so extensively applied were always satisfactory and distinctive, there would be little value attached to any other system of identification. But most analysts are familiar with the fact that, in order to secure these color reactions so generally relied upon, the alkaloids being tested must be in a fairly high state of purity, since the original tests were applied to pure alkaloids: that, in "shaking out" alkaloids by means of immiscible solvents, there is always a considerable amount of foreign matter present in the alkaloidal residue which interferes with many color reactions.

Then again it must be recalled that colorations produced with metallic and many other substances are reactions of the reagent employed and not of the alkaloid. An example of this may be cited in the tests for morphine and codeine with selenous acid.

Finally, the amount of material required to perform a series of color tests on an alkaloidal residue is frequently many times greater than the entire available sample.

A survey of the standard tests for alkaloids indicates that cocaine is the only alkaloid commonly identified by micro-chemical means. The characteristics of its precipitates with such reagents as chromic acid, platinic chloride and potassium permanganate are familiar to all toxicologists and are relied upon for identifying that alkaloid.

While but few alkaloids can be precipitated as easily and in such peculiar forms as cocaine, yet it is safe to predict that a number of very satisfactory tests may be employed in a similar manner for the identification of other alkaloids. With this idea in mind, the writer has been engaged, during the past two years, in an investigation of the precipitates produced by about forty of the alkaloids with some of the common alkaloidal reagents.

The method of procedure differs slightly from that usually employed, in that solution of the alkaloid is made directly on a microscope slide and not in a test tube or flask. In making a microscopic examination of crystals, it is entirely unnecessary to make a solution in a test tube and then use but a few drops for testing. It is also important whether a precipitate is produced in a test tube, the crystals filtered off and then placed on a slide or whether precipitation is made directly on the slide and the precipitate viewed at once through the microscope. The significance of this point will be shown later. A moment's consideration ought to show also that it is just as easy to work with a milligram of alkaloid dissolved in a drop of solvent on a slide as to prepare a 1–100 solution and then use only a drop of the dilution. Moreover, the practical analyst does not have available the large amounts usually prescribed for many of the tests and if he identifies a given alkaloid with a 10 mg. sample that is his good fortune.

In every case the method of procedure in precipitating the alkaloids was the same and essentially as follows: Using a teasing needle or glass rod, transfer a fragment of the alkaloid to a perfectly clean glass slide and drop upon it, from a burette, one drop of $N/10$ HCl. By tapping the end of the slide with the finger, sufficient agitation of the liquid is produced to effect solution of the alkaloid. When all is dissolved, add from a dropping bottle a drop of the appropriate reagent and, without stirring or otherwise

disturbing the mixture, place on the stage of a microscope and examine under the low power. In general, it may be said that the solution of alkaloid must be of such concentration that precipitation on the slide takes place immediately when the precipitant is added. By noting the rate of solution in the acid this may be readily determined in the first trial. If no precipitation takes place at once, set the slide aside protected from dust and make a new precipitation using not necessarily more alkaloid, but a smaller quantity of solvent, in order to obtain a more concentrated solution. In all cases except when using iodine as the precipitant it is advisable to use a slight excess of precipitant, *i. e.*, so that after precipitation the supernatant liquid has a distinct color of the precipitant. In general, it may be stated that when using iodine, only a fraction of a drop of solution should be added in order to secure a crystalline precipitate free from large masses of amorphous precipitate which obscure and prevent the coalition of compound crystals. The reagents used to secure the crystals shown in the accompanying photomicrographs were as follows: $N/10$ iodine, 10 per cent. platinic chloride solution and 5 per cent. palladous chloride solution.

It is well to note that when crystallizing on a flat surface, there will often be fern-like crystal forms along the edge of the field which are due simply to evaporation of liquid and distortion due to the flat surface. The crystals shown in the accompanying photomicrographs were all formed within five minutes after precipitation took place.

ALKALOIDS PRODUCING CHARACTERISTIC CRYSTALS WITH IODINE.

Morphine (Plate 1).—Even the smallest drop of $N/10$ iodine solution produces instantly a dense red-colored precipitate which when viewed at once appears perfectly amorphous under the microscope. Within about a minute, however, the agglutinated masses begin to separate and disclose shining red plates which overlap each other and often extend a third of the distance across the field. In some cases they assume a branch-like appearance but the individual plates can be clearly distinguished.

Codeine (Plate 2).—This alkaloid yields an amorphous precipitate at first as in the case of morphine, but the crystals eventually formed appear much more slowly. Always of a yellow color (never red) they first appear as little blade-like needles which slowly grow in size and send out little branches. The clusters finally formed are much smaller than those of dionin.

Dionin (Plate 3).—This alkaloid (ethylmorphine) is closely related to the above, which is methylmorphine, and as we might expect gives a precipitate very similar to codeine. Here again the crystals are yellow in color, but they are quickly formed, frequently at the first precipitation, and are much larger and more branching than those produced by codeine. If the solution of alkaloid is quite concentrated, a number of compound crystals are sometimes formed which, though much smaller, are very similar to the crystals yielded by the alkaloid heroin with platinic chloride (Plate 14).

The other alkaloids of the morphine group, heroin, apomorphine and narcotine yield amorphous precipitates with iodine which do not become crystalline.

Atropine (Plate 4).—This alkaloid, though yielding oily, amorphous precipitates with a large number of

PLATE 1.
MORPHINE WITH N/10 IODINE × 40.

reagents, forms quite readily a crystalline precipitate with iodine. When first precipitated, the field is simply filled with minute, red, oily globules. After about a minute, however, these little globules begin to elongate and within a few seconds after that process has begun, the entire field is covered with very small red crystals. The latter are fairly uniform in size and show a tendency to form small clusters, though they never unite to form large masses.

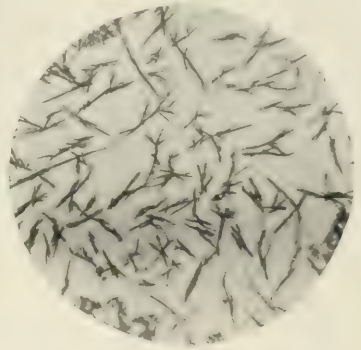

PLATE 2.
CODEINE WITH N/10 IODINE × 40.

ALKALOIDS PRODUCING CHARACTERISTIC CRYSTALS WITH PALLADOUS CHLORIDE.

Morphine (Plate 5).—In a concentrated solution this reagent produces beautifully characteristic clusters of sheaves of crystals with morphine. They are light brown in color and in some cases form so dense a cluster as to appear almost spherical. If the solution is dilute, there is no precipitation at first, but if the slide is observed through the microscope, one may presently see an occasional cluster or bundle of crystals along the edge of the drop. These crystals thus observed along the edge are always much larger than

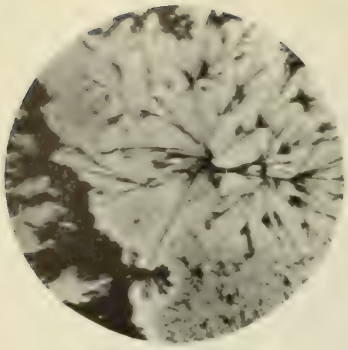

PLATE 3.
DIONIN WITH $N/10$ IODINE × 40.

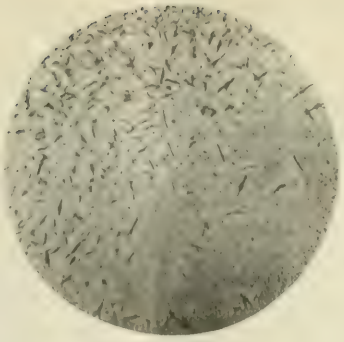

PLATE 4.
ATROPINE WITH $N/10$ IODINE × 40.

PLATE 5.
MORPHINE WITH PALLADOUS CHLORIDE × 40.

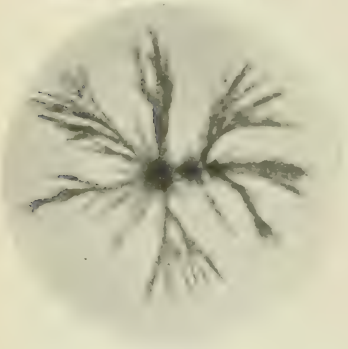

PLATE 6.
CODEINE WITH PALLADOUS CHLORIDE × 40.

PLATE 7.
CODEINE WITH PALLADOUS CHLORIDE × 40.

PLATE 8.
β-EUCAINE WITH PALLADOUS CHLORIDE × 40.

PLATE 9.
COCAINE WITH PLATINIC CHLORIDE × 40.

PLATE 10.
β-EUCAINE WITH PLATINIC CHLORIDE × 40.

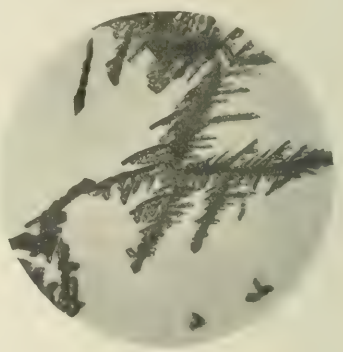

PLATE 11.
NICOTINE WITH PLATINIC CHLORIDE × 40.

PLATE 12.
ANTIPYRINE WITH PLATINIC CHLORIDE × 40.

PLATE 13.
STRYCHNINE WITH PLATINIC CHLORIDE × 40.

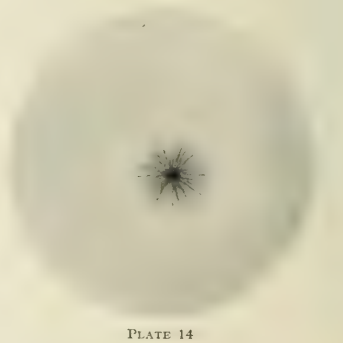

PLATE 14
HEROIN WITH PLATINIC CHLORIDE × 40.

those formed in the center of the drop by reason of concentration due to creeping and evaporation. Whenever this first crystal makes its appearance, however, in this as in all other similar tests, it is usually but a few seconds till a number of other similar crystals make their appearance in other parts of the field. The first one is therefore a good index of the kind of crystal to follow. Though codeine sometimes forms a somewhat similar type of crystals, the latter rapidly grow in size and all tend toward the spherical form.

Codeine (Plates 6 and 7).—This alkaloid forms very peculiar crystals with palladous chloride which rapidly change in appearance. As first precipitated there appear a large number of light brown crystals which are clustered needles arranged in a spherical form very like the crystals of heroin with platinic chloride. This form is transient, however, and the crystals begin to grow in size and density till they assume the appearance shown in Plate 7. When the precipitate is not extremely dense, the crystal still continues to grow and needles become more divided and branching (Plate 6). The latter figure shows the compound crystal in its final form which is decidedly different from that first produced. The behavior of this crystal shows clearly the advantage of watching the development and growth of these crystals from the time the precipitation is first made.

Beta-Eucaine (Plate 8).—Though crystallization is relatively slow, this alkaloid forms highly characteristic crystals of a deep yellow color. The figure represents crystals formed from a concentrated solution. If they were permitted to remain undisturbed they would grow to a size almost twice that shown in the figure. The crystals are very distinct and seldom have more than eight branches.

ALKALOIDS PRODUCING CHARACTERISTIC CRYSTALS WITH PLATINIC CHLORIDE.

Cocaine (Plate 9).—This plate is introduced, not with the idea of presenting a new reaction, but for the purpose of emphasizing the importance of viewing alkaloidal precipitates when first formed. The accompanying photograph was taken immediately after the precipitant was added to the alkaloidal solution, and shows the highly characteristic, feathery crystals by which cocaine may be readily identified. But there is a vast difference in the appearance of these crystals at the end of even a few minutes after precipitation. They lose their delicate structure and while of course retaining a semblance of their former outline, they become more dense and show heavy spines where at first were only delicate feather-like processes. It is significant that while cocaine is the only alkaloid which produces these delicate, feathery crystals, yet other alkaloids also produce precipitates with platinic chloride which are very similar to the large heavy crystals into which the cocaine crystals are gradually transformed. A notable example of this is the alkaloid nicotine (see below).

Beta-Eucaine (Plate 10).—This alkaloid yields, with platinic chloride, crystals which resemble a cluster of little golden flower petals and are highly characteristic. They do not in the least resemble those produced by the near relative of this alkaloid, cocaine. The precipitate, at first amorphous, slowly becomes crystalline and the crystals stand out in bold relief.

Nicotine (Plate 11).—The precipitate which this yields with platinic chloride is often so similar to a large dry crystal of cocaine under similar conditions that they can scarcely be distinguished. It is important to note, however, that the nicotine precipitate takes place only in neutral or faintly acid solution and is soluble in acids. The cocaine precipitate is of course insoluble. The point is well worth remembering when one is examining a preparation of tobacco for the presence of cocaine. When making quick precipitations one may frequently produce crystals with nicotine and platinic chloride as small as those shown in Plate 9, and on the other hand cocaine when precipitated with platinic chloride and the crystals allowed to become dry will often yield crystals very like those shown for nicotine (Plate 11).

Antipyrine (Knorr's) (Plate 12).—Though a synthetic compound which does not occur in nature, yet this well known artificial alkaloid yields, as one might expect, a precipitate with platinic chloride. The crystals are yellow and branching, often quite feathery in appearance.

Strychnine (Plate 13).—This alkaloid forms almost instantly with platinic chloride a great number of characteristic crystals. The peculiar chisel-shaped crystals of strychnine are present and these rapidly assemble to form a cluster. The interesting thing about them is that the clusters are scarcely formed till they suddenly fly apart again, leaving only a number of individual needles. When viewed under the microscope the crystals seem curiously unstable and active. The field is in constant motion with the union and dissolution of clusters. In order to secure a satisfactory photomicrograph, one must almost take a "snap shot." Such crystal forms could never be noted by viewing the dry crystals, filtered from an ordinary precipitation.

Heroin (Plate 14).—This alkaloid, diacetylmorphine, yields with platinic chloride crystals which are as characteristic as those for cocaine. The precipitate as first formed is perfectly amorphous and remains so for fully a minute. Within usually a minute or two, there appear at numerous places on the field, clear circular spaces in the amorphous mass in which are small clusters of needle-like crystals, one cluster in each space. The cluster grows quickly both in size and number of needles until it presents the appearance of a golden yellow spherical mass of spines. Frequently a chain of these clusters will extend across the field. Curiously enough, when the crystal has attained its full size, the needles begin to fly off from the main body as in the case of strychnine, but not so rapidly. These little spines keep splitting off, usually in pairs, until the whole cluster is disintegrated and finally there is nothing left of the original symmetrical cluster but its center, an orange yellow cube of platinic chloride.

The above test is infallible for this alkaloid and is

applicable to the extract obtained after subjecting the alkaloid to the usual "shaking-out" treatment with immiscible solvents, since heroin is not thus decomposed.

Of the common alkaloids which yield *amorphous* precipitates, under the above conditions, with palladous chloride may be mentioned the following: Apomorphine, physostigmine, nicotine, heroin, dionin, narcotine, hydrastine and arecoline.

Amorphous with iodine: Heroin, caffeine (neutral solution), alypin, emetine, narcotine and hydrastine.

Amorphous with platinic chloride: Morphine, atropine, quinine, coniine, codeine, hydrastine, dionin, alypin, aconitine, apomorphine and physostigmine.

With these and other reagents many of the alkaloids yield crystals which are fully as characteristic as those illustrated above. But these will serve to indicate the results which may be obtained.

In many cases, several distinct types of crystals are formed successively by the same precipitate, and such a series of changes has an additional value in determining the identity of any particular alkaloid.

A number of the above alkaloids have been identified by the above reagents in actual unknown samples, and all others have been subjected to the usual scheme of extraction and tests applied to the alkaloidal extract thus obtained. In every case, a satisfactory test was secured on the first extract without necessitating any further purification of the alkaloidal residue.

When not otherwise stated, the photomicrographs here shown were taken when the crystal had just attained its full size and before there was any appreciable evaporation of mother liquor from the slide.

Though the writer is fully aware that it is not customary to mix strong solutions in order to secure satisfactory crystallizations yet the method here employed minimizes the frequency of formation of rosette- or cluster-forms of needles, so common in concentration of an alkaloidal solution. It should be be borne in mind, however, that many reagents will throw alkaloids out of solution, not by the formation of insoluble double salts, but by a "salting-out" action. Many of the slightly soluble alkaloids, such as strychnine, are thus easily precipitated when a drop of salt solution is added to the alkaloidal solution on the slide. When thus precipitated, the alkaloids show a pronounced tendency to assemble in needle clusters, and this behavior is not to be confused with the formation of a true double salt.

The tendency of a number of the alkaloids to form a series of crystal forms may explain, in part at least, the extreme variability of results obtained when volumetric solutions of alkaloidal precipitants are used for the quantitative estimation of alkaloids. If the solution of the alkaloid is fairly concentrated, most of the precipitate is amorphous and slowly becomes crystalline; if dilute, the tendency is toward a crystalline precipitate at once; and the two varieties of precipitate are not, of necessity, identical in composition.

DEPARTMENT OF PHARMACY.
NORTH DAKOTA AGRICULTURAL COLLEGE.

AN IMPROVED METHOD OF ASSAY FOR AROMATIC SULFURIC ACID.[1]

By Linwood A Brown.

Received January 17, 1912.

During the examination of some samples of aromatic sulfuric acid, it was noticed that all the samples were running abnormally low in sulfuric acid, so much so that it made us think that possibly the method might be at fault. Consequently, we began some experiments on the method of assay for this preparation, the results of which are given in this paper, and which we believe will be of some interest to pharmaceutical chemists.

Aromatic sulfuric acid is a mixture of strong sulfuric acid, alcohol, tincture of ginger and oil of cinnamon, and is described by the U. S. P. as follows: "Should contain not less than 20 per cent. by weight, of absolute sulfuric acid, partly in the form of ethylsulfuric acid."

The consensus of opinion appears to be that ethylsulfuric acid is formed even at ordinary temperature when strong alcohol and sulfuric acid are mixed; also that it is hydrolyzed on heating with water or alcohol, but with the exception of Kastle and Frazer, no one seems to have studied its quantitative decomposition by hydrolysis.

It appears to be generally thought that the decomposition must be complete when heated with water, and it appears that the Revision Committee of the U. S. P. 8th held this opinion, for the present method of assay is based upon that theory. The first edition of the U. S. P. 8th, in the assay of this preparation required it to be boiled with 30 cc. water "for a few minutes;" the later editions, "with additions and corrections to June 1, 1907," extend this time of heating to 4 hours. Ethyl sulfuric acid is stated to be more easily decomposed than its salts, in fact the salts of this acid are considered as not being hydrolyzed on heating. This view is contradicted by the work of Kastle and Wilkie[2] in their work "On the

TABLE A.

No.	Time of heating.	Cc. of H_2O.	Per cent. H_2SO_4. U. S. P. Method.
1	4 hours	30	18.40
2	4 "	30	18.40
3	None	..	13.35
4	2 hours	30	15.44
5	4 "	30	16.81
6	6 "	30	17.83
7	8 "	30	19.02
8	4 "	30	16.81
9	4 "	60	16.46
10	4 "	90	16.35
11	4 "	120	15.77
12	4 "	150	15.53
13	4 "	300	14.81

TABLE B.

No.	Per cent. free H_2SO_4.	Per cent. H_2SO_4 as ethyl sulfuric.	Total H_2SO_4.	Gms. $BaSO_4$ (direct).	Time of heating.	$BaSO_4$ (additional).	Date of assay.
14	16.89	3 29	20 18				7/1/11
15	6 92	12 81	19 73				12/6/11
16	6 94	12 86	19 80				
17	6 95	12 59	19.54	0.1518	1 hour	0.0033	
18	6.98	13 05	20.03	0.1509	2 hours	0.0048	
19	7 00	12 99	19.99	0.1520	3 hours	0.0044	
20	6 94	12 82	19.76	0.1503	4 hours	0.0046	

[1] Presented at A. C. S. Meeting at Washington, D. C., December, 1911

[2] Unpublished—Thesis for B.S. degree, Ky. State Univ., 1904.

Decomposition of Barium Ethyl Sulfate." They, however, were studying the effect of the halogen salts upon the barium ethyl sulfate, which has very little bearing upon the conditions present in this paper.

The salts of ethyl sulfuric acid are soluble; even the barium salt is soluble, while any free sulfuric acid is precipitated as the sulfate, the barium ethyl sulfate remaining in solution. It is upon this feature that we have endeavored to work out a method for the determination of the total sulfuric acid in the aromatic sulfuric acid, U. S. P.

METHOD OF ANALYSIS.

After making up my standard sample of aromatic sulfuric acid, containing a known amount of sulfuric, I then assayed it by the U. S. P. method with the results shown in Exps. 1 and 2, and did not recover all of the sulfuric acid. Now, the next thing to do was to devise a method which would yield the total acid present. After a number of ideas were tested out, we finally decided upon the following method:

A sample of about 10 grams was weighed out and diluted with water to exactly 100 cc.; 10 cc. aliquots were taken and the total acidity determined by titrating against decinormal KOH, using phenolphthalein as indicator. This gave us the acidity due to free sulfuric acid and to ethyl sulfuric acid. The neutralized sample was then diluted to a volume of 100 cc., then quickly heated to boiling over a free flame, 2 cc. hydrochloric acid added, followed by an excess of barium chloride solution; the solution was boiled for an additional minute or two, then placed on the water bath and heated for one hour. The precipitate of $BaSO_4$ was filtered off, washed well, ignited and weighed.

CALCULATION OF RESULTS.

Grams $BaSO_4 \times 0.42$ = grams H_2SO_4 in form of free sulfuric acid, divided by 0.0048675 = cc. of decinormal KOH required to neutralize free sulfuric acid.

Cc. $N/10$ KOH consumed in total acidity determination, minus cc. equivalent of free H_2SO_4 equals cc. $N/10$ KOH required to neutralize ethyl sulfuric acid.

As ethyl sulfuric acid is a monobasic acid, multiply the number of cc. for ethyl sulfuric by $2 \times 0.0048675 \times 10 \times 100$ and divide by weight of sample, equals per cent. of sulfuric acid in sample in the form of ethyl sulfuric acid.

Grams free sulfuric $\times$ 10 $\times$ 100, divided by weight of sample equals per cent. of free sulfuric.

This method was tried out on the standard sample, with the results shown in Exps. 14–16.

In samples that have been allowed to stand several months a small amount of the sulfuric acid is converted into the di-ethyl sulfate and which is not determined by this method; this, however, is very small, amounting to only about 0.4 per cent. H_2SO_4 in five months, under the conditions existing in the U. S. P. preparation.

In 1898, Kastle and Frazer, in an unpublished work (Thesis for Master of Science degree, Ky. State Univ.), studied the hydrolysis of sulfuric ethers, and came to the conclusion that ethyl sulfuric acid is hydrolyzed to a greater extent in concentrated than in dilute solutions.

Experiments 8–13 show the effect of dilution upon the hydrolysis of ethyl sulfuric acid, the time of heating being constant throughout the series.

Experiments 3–8 show the effect time of heating has upon the hydrolysis, the dilution remaining constant throughout the series.

In order to see what effect heating would have upon the barium ethyl sulfate, in separating the free sulfuric from the ethyl sulfuric acid in the proposed method, Experiments 17–20 were run as follows:

After the sample was neutralized by the standard alkali, rendered acid by hydrochloric and an excess of barium chloride added, the sample was heated on the water bath for 20 minutes, or just long enough to enable us to filter off the precipitated barium sulfate, after which the filtrates were heated for 1, 2, 3, and 4 hours longer, and any additional barium sulfate formed was filtered off and weighed up separate from the main bulk of the precipitate. Reference to Table B will show that practically no hydrolysis of the barium ethyl sulfate took place, as the small amount of barium sulfate obtained after heating remained fairly constant. The author believes that the additional amount of barium sulfate, thus obtained, was largely, if not entirely, due to the difficulty of removing the finely precipitated barium sulfate after only 20 minutes' heating, and not to any hydrolysis of the barium ethyl sulfate.

Table C shows the analysis (by both the U. S. P. and the proposed method) of some samples of aromatic sulfuric acid, as found in drug stores.

TABLE C.

		Brown's method.		
Experiment No.	Per cent. H_2SO_4. U. S. P. method.	Per cent. free H_2SO_4.	Per cent. H_2SO_4 as ethyl sulfuric.	Per cent. total H_2SO_4.
33,860	14.46	8.35	10.94	19.29
33,862	15.28	7.71	14.74	22.45
33,884	12.50	6.12	9.47	15.59
33,887	14.87	6.43	13.82	20.25
33,889	18.79	13.45	12.60	26.15
33,894	16.44	8.37	12.96	21.33
33,910	16.69	6.72	14.14	20.86
33,970	17.63	7.77	15.30	23.07
33,974	18.14	6.93	14.58	21.51

CONCLUSION.

1. The U. S. P. method of assay does not give the total amount of sulfuric acid present.

2. Ethyl sulfuric acid is hydrolyzed to a greater extent in concentrated than in dilute solutions.

3. The hydrolysis of ethyl sulfuric acid is not complete, even after 8 hours' heating, but does increase with the length of time of heating.

4. That a small amount of di-ethyl sulfate is formed after a few months in the aromatic sulfuric acid, and is not determined by either the U. S. P. or by the proposed method.

5. That the proposed method of assay gives more accurate results, closely approaching the theoretical amount of sulfuric acid present.

6. That the proposed method of assay shows the

amount of esterification that has taken place in the sample.

7. That barium ethyl sulfate is not hydrolyzed in dilute slightly acid aqueous solution, to any appreciable extent.

In conclusion, I wish to give credit to J. M. Humble for his assistance to me in conducting the experimental part of this work.

KENTUCKY AGRICULTURAL EXPERIMENT STATION.

A METHOD FOR ASSAYING SPIRITS OF CAMPHOR.

By ARTHUR T. COLLINS.

Received February 29, 1912.

Spirits of camphor can be assayed, and the percentage of camphor very accurately determined, by the use of the polariscope. It has been long known that camphor is optically active, some camphors rotating the plane of polarization to the right, and some to the left. The amount of this deviation will vary in camphors coming from different localities, or even from the same locality.

Most camphors are dextro gyrate, a 10 per cent. solution giving in a 200 mm. tube an angle of 8°, more or less. In order to know the percentage of camphor in a solution, it will be necessary to know the rotation angle of the particular camphor that was used in making up the solution. This can be done by taking 50 cc. or more of the spirits of camphor, and evaporating on a water bath; by this operation the camphor can be obtained free from alcohol or moisture. Of course there is a considerable loss of camphor, often as much as 30 to 40 per cent. but the camphor that remains has exactly the same rotation as the original.

The camphor obtained by evaporation on the water bath contains all the non-volatile impurities that were in the original solution, and in order to get rid of these, the camphor is transferred to a watch glass of about 7 or 8 cc. diameter, having for a cover a glass funnel of the same diameter—both funnel and watch glass having ground edges. The apparatus is placed over a low flame, and the camphor sublimed on to the funnel.

We have now the pure camphor that went to make up the original solution. This is made up to a 10 per cent. solution in a 25 cc. volumetric flask, and used as a standard for the determination of the camphor in the spirits of camphor in question. The method is very accurate and the entire operation may be accomplished in two hours time.

Using camphors from different sources made up to 10 per cent. solutions, the results are as follows:

	Rotation in minutes.	Per cent.
Sample A.....	482.8	9.94
Control.....	485.3	
Sample B.....	488.5	10.003
Control.....	488.3	
Sample C.....	492.5	10.01
Control.....	491.7	

If the original gum camphor has been impure, or if optically active substances have been added to increase the rotation, these may be found on the watch glass, after the camphor has been sublimed, and can then be weighed or investigated.

In case sugar has been added, this will be found by evaporating in a drying oven at a temperature of 105° C. After all smell of camphor is gone the sugar should be made up to volume with water, and the amount of rotation deducted from the optical rotation of the original spirits.

The entire method is as follows:

Polarize in a 200 mm. tube, making correction for temperature by adding $^1/_2$ minute for every degree C. above 20° C., and deducting same amount below 20° C. Take the mean of 10 readings, place 50 cc. or more of the spirits in an evaporating dish on water bath, using cold air jet if convenient, to facilitate evaporation. Just before the camphor solidifies, stir with glass rod, so that it may become dry as soon as possible. When quite dry place on watch glass having funnel cover, over a low flame, with wire gauze between, and fitting closely to the bottom of the watch glass.

When the camphor is entirely sublimed, remove the pure camphor from the funnel, take $2^1/_2$ grams of this, make up with alcohol in a 25 cc. flask, polarize as in the first case; this is called the "control." The percentage is found by dividing the minutes of rotation of the control into minutes of rotation of the original sample, multiplied by ten.

SWARTHMORE, PA.

SUGGESTED MODIFICATIONS TO THE U. S. P. ASSAY OF OPIUM.[1]

By R. NORRIS SHREVE.

Received January 17, 1912.

The Pharmacopoeia directs for the determination of Morphine, an aqueous extraction of the opium, concentration of these extracts, precipitations of the morphine from a weak alcoholic solution, and determination of the impurity in the precipitated morphine by weighing of the substance insoluble in lime-water. As thus carried out the method gives results that are not accurate. There are the following sources of error:

1. Incomplete extraction of the opium.

2. Retention of morphine by the mother liquor during precipitation.

3. Inaccuracies in the lime water method for determination of the impurities in the precipitated morphine.

INCOMPLETE EXTRACTION OF THE OPIUM.

The Pharmacopoeia directs for the extraction: Agitation every ten minutes (or continuously in a mechanical shaker) during three hours, followed by filtration, washing, re-agitation, and re-washing. In case of certain opiums this procedure will not exhaust the opium of its morphine as is shown in Table I.

Comment on Table I.—The three samples of opium were of Turkish grade and of a moderately fine powder. In every case ten grams were used for assay. Instead of determining the purity of the crude morphine by the lime water method as the U. S. P. directs, the more accurate but slightly longer Mallinckrodt

[1] Presented at the A. C. S. Meeting at Washington, D. C., December, 1911.

TABLE I.

No.	Outline of extraction, U. S. P. Method except as indicated.	Weight of crude precipitated morphine. Grams.	Purity of crude by Mallinckrodt re-assay.[1] Per cent.	+ correction for solubility of morphine in U. S. P. mother liquors. Grams.	Pure morphine. Per cent.
		Opium sample 1.			
1	In mechanical shaker for 8 hrs.	1.5875	94.6	0.052	
	Marc of preceding reextracted.	0.3185 } 1.906		0.024 } 0.076	18.79
2	Extracted 3 times in shaker.	1.909	93.0	0.0635	18.39
3	Opium triturated in mortar, then put in shaker; marc of preceding re-extracted.	1.6265 } 1.7515			
		0.125 }			
4	Extracted shaker; Lamar[2] modification applied	1.3125	94.6	0.060	13.02
5	Opium + 45% lime, extracted, acidified; Lamar modification applied	2.097	88.7	0.055	19.16
		Opium sample 2.			
6	In mechanical shaker for 8 hours.	0.988	90.6	0.050	9.45
7	Duplicate.	1.030	91.8	0.51	9.96
8	In very rapid shaker for 12 hours.	1.623	89.3	0.060	15.11
		Opium sample 3.			
9	In mechanical for 8 hours.	0.914	91.3	0.051	8.86
10	Duplicate.	0.960	91.1	0.051	9.26
11	In very rapid shaker for 8 hours.	1.668	89.6	0.052	15.46
		Opium sample 4.			
12	In mechanical for 8 hours.	0.987	93.7	0.051	9.76
13	Duplicate.	0.990	91.4	0.051	9.56
14	In very rapid shaker for 8 hours.	16.55	90.6	0.052	15.51

[1] Proc. A. O. A. C. 23rd convention, Bur. Chem., *Bull.* **105,** 128 (1906).
[2] *Am. J. Pharm.*, **71,** 36 (1900).

re-assay was used. This re-assay is carried out as follows:

Morphine up to 2 grams is mixed with 0.5 gram of freshly slaked lime, and 18 cc. of water added, rotated occasionally during half an hour, filtered without suction (suction causes foaming), and washed with lime water until the filtrate weighs 35 grams: 3 cc. of alcohol added, flask rotated; 20 cc. of ether added, flask rotated again; finally 0.5 gram of ammonium chloride added, and the flask shaken for ten minutes: set aside for 2 hours (or over night) for the morphine to precipitate. Morphine filtered and washed, in the manner which the U. S. P. directs in case of the crude morphine. Correction for the morphine soluble in alcoholic mother liquors is determined by blank assay on pure morphine. The "+ correction for solubility of morphine in U. S. P. mother liquors" was obtained likewise by running a blank precipitation, but of course under the conditions parallel to the U. S. P. assay.

The opium of sample 1 was not completely exhausted of its morphine by the aqueous extraction, as is readily seen from Experiments 1 to 4 of Table I. However, in Experiment 5, which was a lime assay, the opium was exhausted as determined by test on the marc. The details of this experiment are as follows: 10 grams opium were mixed with 4.5 grams of lime, and triturated with 100 cc. water for several hours, filtered and washed with water sufficient to make filtrate measure 150 cc.; retriturated and rewashed; filtrate acidified with dilute hydrochloric acid, concentrated, and inorganic matter, etc., thrown out by alcohol (Lamar Modification, *Loc. cit.*); alcohol evaporated and morphine precipitated as U. S. P. directs.

The opium of samples 2, 3 and 4 was exhausted of only about $^2/_3$ of its morphine by gentle mechanical shaking for 8 hours. By employing a mechanical shaker making three strokes a second, it was possible to exhaust the opium.

Such being the case with some opiums, I always test the marc for completeness of extraction; for this, the following test is satisfactory: Wash the marc with an additional 100 cc. of water; evaporate the filtrate to about 2 cc., filter, add 4 cc. of washed ether, and ammonia to faint alkalinity. If the morphine was not all exhausted in the regular extraction, it will precipitate here in well defined crystals which give the characteristic color reactions. The precipitation is facilitated by scratching the inside of the test tube with a glass rod. I suggest that opium always be tested for completeness of extraction of its morphine, and that the Pharmacopoeia Revision Committee embody some such test as the one just given in the official method, with directions to repeat the assay using more vigorous shaking and more washing in case the test shows morphine in the marc. This repeating will be generally necessary, as by the time the result of the test is obtained the morphine in the assay will have been precipitated, since it is not worth while to wait for a test which will indicate morphine in the marc in only an occasional opium.

In case of the U. S. P. powdered opium, the substances used by the manufacturers to standardize the opium often retard the extraction of the morphine, so that in assay of opium of this kind, it is especially necessary to apply tests to determine completeness of extraction. Because of this difficulty of extracting some opiums, an aliquot part method for the assay of this drug is not advisable as one could never be sure of the relative amount of morphine in that part taken for assay.

RETENTION OF MORPHINE BY THE MOTHER LIQUORS DURING PRECIPITATION.

It is well known that the alcoholic mother liquors employed during the precipitation of the morphine hold in solution some of the morphine. This has been pointed out by many workers especially in the co-operative work on opium assaying, done during the leadership of the Bureau of Chemistry.

The amount of pure morphine retained by solvents present when the morphine is precipitated in the

U. S. P. assay is easily obtained by dissolving one and one-half grams of morphine in 5.5 cc. $N/1$ sulfuric acid and water sufficient to weigh 20 grams; then precipitate under the conditions of the U. S. P. Table II gives results of such blank precipitations.

TABLE II.

No.	Amt. of morphine taken. Grams.	Amt. of morphine recovered. Grams.	Amt. of morphine retained by mother liquors. Gram.	Temperature during precipitation. Centigrade.
1	1.500	1.459	0.041	0°
2	1.500	1.443	0.057	20°
3	1.500	1.428	0.072	26°
4	1.500	1.426	0.074	26°

Comment on Table II.—In case of No. 4, instead of dissolving the morphine in 5.5 cc. of normal acid, there was used 16.5 cc. to ascertain if the decrease of free ammonia and the increase of ammonium salts would have an appreciable effect on the morphine retained; the result shows no effect. The length of time for precipitation was over night, though for the blanks themselves one or two hours is sufficient.

The corrections for solubility of morphine in Table I were determined by such blanks run parallel to the opium precipitation. There is no doubt, however, that the extractive matter in opium has an influence on the amount of morphine thus retained. To obtain some evidences on this point the following experiments were conducted:

Two assays were run: No. 1 on 10 grams of opium in the regular way; No. 2 on 100 grams of opium, using 10 times the quantities of solvents, etc. Both assays were precipitated under the same conditions: No. 1 gave 1.624 grams of crude morphine, reassaying 80.2 per cent. pure and, hence containing 1.302 grams pure morphine; No. 2 gave 16.007 grams of crude morphine, re-assaying 81.1 per cent. pure, and hence contained 13.0 grams pure morphine. Thus both gave the same percentage of morphine.

The mother liquors of No. 2, the 100 grams assay, were analyzed for morphine by this method: Made slightly acid, evaporated, mixed with excess of slaked lime and the cake exhausted of its morphine. The lime water filtrates were extracted with benzole to remove non-phenolic alkaloids, then acidified, evaporated to small volume, alcohol added to throw out inorganic matter, filtrates plus washings heated to drive off alcohol. Now morphine completely extracted with amyl alcohol, after making alkaline; amyl alcohol extracted with 10 per cent. sulfuric acid, and morphine precipitated by ammonia. The purity of this morphine was determined by Mallinckrodt re-assay: result, 1.15 grams of morphine alkaloid which remained dissolved in the mother liquors. This corresponds to 0.115 gram for regular U. S. P. mother liquors. A parallel blank on pure morphine indicated a correction of 0.069 gram, so it is apparent that in this case the extractive plus the solvent present held back considerably more morphine than is represented by the dissolving power of the solvents themselves.

This analysis of the U. S. P. mother liquors was very tedious, yet it should be carried on the mother liquors of assays from a number of different opiums before we can say just how much morphine is retained in the precipitation mother liquors. The chloroform alcohol method of Eaton[1] could probably be used and would be simpler.

Of course it would be better to use an immiscible solvent method for the assay of morphine and thus avoid altogether this retention of the morphine in the mother liquors of the U. S. P. assay. I have successfully used an amyl alcohol extraction, but the method is tedious and long. It gives results agreeing with the modified U. S. P. method as was used for the assays of Table I.

The chloroform alcohol extraction method of Eaton looks very promising, but I would suggest, because of the difficulty in extracting opium, that instead of an aliquot part extraction of the opium, a complete lime extraction be employed. This indeed works very nicely, and to carry it out I mix with the opium 40 per cent. of its weight of lime and extract with lime water. Furthermore it would be advisable to collect a sufficient quantity of the morphine from the evaporation of the chloroform alcohol, and compare the purity by titration against the accurate Mallinckrodt re-assay (run with blank to determine morphine in the mother liquors).

INACCURACIES IN THE LIME WATER METHOD FOR DETERMINATION OF THE IMPURITIES IN THE PRECIPITATED MORPHINE.

These inaccuracies were pointed out by Kebler in the above-mentioned coöperative work under direction of the Bureau of Chemistry. My experience has been that the lime water method gives results that are from 3–7 per cent. higher than the truth, the error varying with the nature and amount of impurity with morphine. This variation in the impurity depends on the sample of opium and the treatment it has been subjected to, such as temperature during and upon the conditions of the assay.

The only satisfactory method for the determination of the purity of crude morphine in the U. S. P. and similar assays is the Mallinckrodt re-assay. Two objections have been brought against this method, namely (*a*) time involved, (*b*) correction for morphine in mother liquors.

In the hands of several chemists, whom I have observed, the extra time necessary over that required by the lime water method is the 15 or 20 minutes it takes to filter and wash the precipitated morphine from the re-assay. On the other hand it is neither essential to use counterbalanced or tared filter papers for filtration of the crude morphine, nor is it worth while to dry the crude morphine. After washing the crude morphine, suck it nearly dry, and then remove it to a small Erlenmeyer flask for solution in excess of lime, and filter through the same filter paper.

The corrections for morphine dissolved in the re-assay mother liquors can readily be obtained from blanks on pure morphine. This correction varies with temperature and slightly with individual manipulation. After a series of corrections for the conditions are determined, it is no longer essential to run a blank as the variations under ordinary conditions are relatively small. Table III gives a series

[1] Bur. Chem., *Bull.* **137**, 188 (1910).

of blanks for different temperatures. The morphine used was purified by twice crystallizing from Columbian spirits and the alkaloid obtained by precipitating a solution of sulfate of morphine.

TABLE III.

No.	Amt. of morphine. Grams.	Amt. of morphine recovered. Grams.	Amt. of morphine retained by mother liquor Gram.	Temperature during precipitation. Centigrade.
1	1.500	1.482	0.018	17°
2	1.500	1.481	0.019	22°
3	1.500	1.4745	0.0255	27°
4	1.500	1.474	0.026	29°

CONCLUSION.

We have discussed (1) the difficulty of completely extracting morphine from opium; (2) the amount of morphine retained by the alcoholic mother liquors of the U. S. P. method; (3) the determination of the purity of the crude precipitated morphine.

It is suggested (1) that a test always be applied to determine the completeness of the removal of the morphine; (2) that a correction be added for morphine dissolved in the mother liquors of the U. S. P. opium assay. and that provisionally a blank on pure morphine be made to determine this correction; (3) that the Mallinckrodt re-assay be used to determine the purity of the crude morphine.

It gives me pleasure, in connection with this paper, to acknowledge my indebtedness to the Lamar Chemical Works and to the Mallinckrodt Chemical Works.

LAMAR CHEMICAL WORKS,
NEWARK, N. J.

A NOTE ON THE DETERMINATION OF THE DIGESTIVE VALUE OF PAPAIN.

By J. R. RIPPETOE.

Received January 11, 1912.

H. T. Graber in a recent article (THIS JOURNAL, Dec., 1911, p. 919) gives a method for determining the digestive value of papain, using fine ground steak in 0.3 per cent. hydrochloric acid solution and comments as follows: "Some manufacturers claim that the test should be conducted in an alkaline media and that egg albumen should be used instead of raw beef; but to me this seems as absurd as to claim that pepsin should be tested upon starch in an alkaline media."

For several years this laboratory has employed a method for determining the digestive value of papain using egg albumen in an alkaline media. It might be of interest to note some results obtained by this method.

Method.—Prepare egg albumen as directed under pepsin assay U. S. P. 8th revision. Introduce into a 4-oz. wide-mouth flint bottle 40 cc. of a 0.1 per cent. sodium hydroxide solution and add 10 grams of the disintegrated albumen; stopper the bottle and shake vigorously until the albumen is broken up. Then add the papain in fine powder and mix by shaking gently for 15 seconds. Place the bottle in a water bath previously heated to 52° C. and digest at this temperature for 6 hours, removing the bottle every 10 minutes and shaking gently for 15 seconds. At the end of this period transfer the mixture to a 100 cc. graduated stoppered cylinder, rinse the bottle with water, add the rinsings to the mixture and make the volume up to 70 cc. with water. Set the cylinder aside and after standing for 1 hour read off the volume of the deposit. The deposit may be read a second time after standing 16–18 hours (over night) which seems to give more positive results, especially if the volume is large.

The results of the assay of five samples by the above method are recorded in the following tables:

TABLE I.

Sample.	Deposit read after standing: 1 hr. Cc.	16 hrs. Cc.
Blank	52.0	43.0
A 0.1 gram papain	26.0	18.0
A 0.2 gram papain	8.0	8.0
B 0.1 gram papain	41.0	31.0
B 0.2 gram papain	36.0	18.0

The blank consisted of 10 grams of the disintegrated albumen in 40 cc. of the alkaline solution without the addition of papain and was carried through the digestion and agitation in the same manner as the tests containing the papain.

Sample A was assayed in an acid media using 0.2 grams of papain in fine powder with the results as shown in Table II:

TABLE II.

	Deposit read after standing: 1 hr. Cc.	16 hrs. Cc.
0.1 per cent. HCl solution	16.0	20.0
0.2 per cent. HCl solution	30.0	30.0
0.3 per cent. HCl solution	32.0	30.0

TABLE III.

	Deposit read after standing: 1 hr. Cc.	16 hrs. Cc.
C 0.1 gram papain	15.0	12.0
C 0.2 gram papain	3.0	5.0
D 0.1 gram papain	25.0	23.0
D 0.2 gram papain	13.0	12.0

TABLE IV.

	Deposit read after standing: 1 hr. Cc.	16 hrs. Cc.
C 0.1 gram papain	2.0	3.0
C 0.2 gram papain	0.8	1.0
E 0.1 gram papain	5.0	5.5
E 0.2 gram papain	1.0	1.5

It might be said that Sample A, Table I, had twice the digestive value of Sample B, since the deposit from 0.1 gram A was the same as the deposit from 0.2 gram B, reading after 18 hours.

The results shown in Table II indicate that some digestion takes place in 0.1 per cent. HCl but 0.2 or 0.3 per cent. inhibits the action of the ferment.

The variation in the volume of the deposit obtained with Sample C, as shown in Tables III and IV, is possibly due to the varying composition of the albumen of the eggs used, and suggests the advisability of using a standard sample of papain for comparison when making an assay of an unknown sample upon egg albumen.

The method is also applicable for determining the digestive value of pineapple juice. A sample of dry

pineapple juice, using 1 gram of dry juice, neutralized with sodium hydroxide, to 10 grams of the albumen required 35 cc. of 1 per cent. sodium hydroxide solution, with 3 hours' digestion, left a residue of 2 cc., reading after 18 hours, while a blank read 41 cc.

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THE BROMINE AND IODOMETRIC METHODS FOR THE VOLUMETRIC DETERMINATION OF CRESOL.[1]

By C. M. PENCE

Received January 17, 1912.

Of the several methods suggested for the volumetric determination of phenol, the bromine method has received the most consideration, and in almost every instance where bromine has been used an attempt has been made to substitute iodine in its stead.

The popularity of the bromine method is no doubt due to two causes: First, to the fact that it answers the demand for a reliable method in the determination of the first member of the series, namely, phenol; second, to the ease in manipulation resulting from the use of the Koppeschaar bromine solution.

Now cresol is the next member of the homologous series; however, it presents, upon treatment with bromine solution and acid, problems quite different from that of phenol. Since commercial cresol is a mixture of the three isomeric phenols *o*-, *m*- and *p*-cresol, the presence of the CH_3 group in the different positions necessitates the formation of compounds structurally unlike and empirically the same, and also causes, in the case of meta cresol, the formation of compounds both structurally and empirically different from those formed by *o*- and *p*-cresols. In 2,4,6-tribrom phenol brom, the bromine occupies both the *o*- and *p*-positions. Now in the case of *o*- and *p*-cresol the CH_3 group occupies the *o*- and *p*-positions and only dibromcresol and dibromcresol brom compounds can be readily formed since the CH_3 group is more difficult to replace by free Br than is a hydrogen atom. However, the CH_3 group is slowly replaced and prolonged standing (several days) results in formation of tribromphenol brom—W. Autenrieth and F. Beuttel[2] have recently published the results of an extensive investigation along this line.

Meta cresol forms tribrom-*m*-cresol brom since the CH_3 group is not in the position that the Br atom would occupy.

H. Ditz and F. Cedivoda[3] have proposed a bromine method for cresols depending upon the difference in speed of reactions between bromine and *m*-cresol on the one hand and bromine and *o*- and *p*-cresols on the other. If either *o*- or *p*-cresol is mixed with a known excess of bromine solution, acidified with (1 : 1) hydrochloric acid and agitated for 1 min., on adding KI and titrating with thiosulfate it will be found that each molecule of *o*- and *p*-cresols has absorbed 2 atoms of bromine. Under the same conditions each molecule of *m*-cresol will absorb 3 atoms of bromine. Now if acidification is effected by concentrated sulfuric acid, the solution shaken for five minutes and insoluble matter removed by filtration, 3 atoms of bromine will have combined with each molecule of *o*- and *p*-cresol, 4 atoms with each molecule of *m*-cresol.

The above method depends for its success upon definitely fixed conditions; namely: time, strength of acid, excess of bromine, etc. F. Russig and G. Fortmann[1] have criticized this method and H. Ditz[2] has replied at length.

The present study of the reaction of bromine and iodine upon the different cresols was made for the purpose of finding which of the cresols were amenable to assay by processes which do not require previous knowledge concerning the percentage of product, that is, by processes dependent upon the formation of definitely fixed, comparatively stable, final products; namely: compounds containing three atoms of bromine in combination.

Samples of the individual cresols were redistilled and volumetric solutions prepared from the distillates, small amounts of $N/2$ NaOH being added to facilitate solution. Aliquot portions of these solutions were used in the several determinations.

The results appearing in the tables are based upon the formation of dibromcresol brom and tribrom compounds on the one hand and diiodo compounds on the other.

ORTHO CRESOL.

No.	Cc. Ortho cresol.	Cc. $N/10$ Br.	Cc. H_2O.	Cc. Conc. HCl.	Time of standing.	Cc. 20% KI.	Cc. Conc. HCl.	Time of standing. Hrs.	Results. Per cent.
1	20	50	175	5	20 min.	10	–	1½	94.45
2	20	50	175	5	1½ hrs.	10	–	1½	103.5
3	20	50	175	5	1½ hrs.	10	–	2½	102.7
4	20	50	175	5	1½ hrs.	30	–	3½	101.1
5	20	50	275	5	1½ hrs.	20	–	2	100.98
6	20	50	275	5	1½ hrs.	20[1]	–	2	100.68
7	20	50	275	5	1½ hrs.	20	–	14	99.78
8	20	50	275	5	1½ hrs.	30	–	2	99.98
9	20	50	275	5	1½ hrs.	30	–	3½	100.17
10	20	50	275	5	1½ hrs.	30	–	4½	99.95
11	20	75	275	5	1½ hrs.	20	–	2	109.4
12	15	50	275	5	1½ hrs.	30	–	18	105.15
13	10	50	275	5	1½ hrs.	30	–	18	106.85
14	15	50	275	5	3 hrs.	30	–	5 min	113.3
15	15	50	275	2.5	5 hrs	30	–	18	106.9
16	10	50	275	2.5	4 hrs.	30	5	20	93.4
17	15	50	275	2.5	5 hrs.	30	5	40	86.22

No.	Ortho cresol. cc.	$N/10$ I. cc.	g. $CH_3COONa.3H_2O$.	Time of standing.	Procedure.	Result. Per cent.	Excess $N/10$ I, cc.
18	25	50	5	30 min.	Diluted, added 5 cc.	93.66	±25
19	25	50	5	1¼ hrs.	$CHCl_3$, titrated with	100.04	±25
20	25	50	5	14 hrs.	N/10 thiosulphate,	100.71	±25
21	25	50	9	1 hr.	using starch as in-	99.93	±25
22	25	50	9	2 hrs.	dicator	100.1	±25

Ortho cresol does not readily form a stable dibrom-*o*-cresol brom or a tribrom compound as is evidenced in Exp. 1. However, upon 1½ hours' stand-

[1] Read at A. C. S. meeting at Washington, D. C., December, 1911.

[2] "Ueber die Bestimmung des Phenols, Salicyl alkohols, der Salicylsäure und *p*-oxybenzoësäure als Tribrom phenol brom" (Autenrieth und Beutel), *Archiv der Pharm.*, **1910**, 112.

[3] "Reactions of Bromine with Phenol and the Cresols, a Process for Calculating the Composition of Mixtures Thereof" (Ditz and Cedivoda), *Z. angew Chem.*, **1899**, 873 and 897. Abstr.—*Analyst*, **25**, 74.

[1] "Estimation of Cresol" (Russig and Fortmann), *Z. angew. Chem.*, **1901**, 157–60. Abstr.—*J. Chem. Soc.*, **1901**, II, 289.

[2] "Estimation of Cresol" (H. Ditz), *Z. angew. Chem.*, **1901**, 160–5. Abstr.—*J. Chem. Soc.*, **1901**, II, 289.

[3] Heated to 40° C. after addition of KI.

ing more than sufficient Br is absorbed for the formation of these compounds and the addition of 10 to 30 cc. of 10 per cent. KI with from $1^1/_2$ to $3^1/_2$ hours' standing does not result in the liberation of the bromine necessary for the formation of either dibrom-*o*-cresol or a tribrom compound as would occur if reaction proceeded in a manner strictly analogous to phenol (Exps. 2, 3, and 4).

Now a greater dilution results in the absorption of a smaller quantity of bromine but results are still too high, Exps. 5 and 6. Increased standing after addition of 20 cc. 20 per cent. KI causes a reversal with practically theoretical quantities of bromine absorbed, the time of standing being materially reduced upon increase in the quantity of KI (Exps. 7, 8, 9 and 10).

An increase in concentration of bromine in contact with *o*-cresol as is effected by larger quantities of Br solution or a decrease in the quantity of cresol solution results in the absorption of much more than the theoretical quantity of bromine and even upon prolonged standing in contact with increased quantities of KI, suitable reversal does not take place (Exps. 11, 12, 13, 14 and 15).

The effect due to increase in the quantity of acid is very marked. When bromine is liberated by one-half the usual quantity of concentrated HCl sufficient reversal does not take place after addition of KI (Exps. 14 and 15). However, when an additional 5 cc. of concentrated HCl are added at the same time as the KI, the reversal causes far less than theoretical quantities of bromine to remain in combination (Exps. 16 and 17).

Thus it will be seen that practical results dependent upon the formation of a dibromcresol brom or tribrom compound can not be obtained except by definitely fixing the several conditions of the experiment in pursuance of which a previous knowledge of the percentage of *o*-cresol is required.

Now when iodine acts upon *o*-cresol, diïodo-*o*-cresol is formed. The reaction is reversible and sodium acetate is added to unite with the hydriodic acid produced by the substituting iodine, thereby causing the reaction to proceed to completeness (Exps. 18, 19, 20, 21 and 22). In this case, the reaction ends with the formation of the diïodo compound, hence it is made the basis of the following method for the determination of *o*-cresol.

Dissolve 2–2.5 g. *o*-cresol in distilled water containing about 10 cc. $N/2$ NaOH to facilitate solution. Dilute to 1000 cc. Withdraw 25 cc. portions and place in a 500 cc. glass stoppered receptacle. Add to the receptacle approximately 9 grams sodium acetate and then 50 cc. $N/10$ I solution. Let stand 1 hour, dilute with 100–200 cc. distilled water, add a few cc. of $CHCl_3$ to dissolve the precipitated diïodocresol and titrate with $N/10$ thiosulphate, using starch as an indicator.

1 cc. $N/10$ I = 0.002681 g. *o*-cresol.

Meta cresol does not rapidly form tribrom-*m*-cresol brom with the subsequent formation of tribrom-*m*-cresol upon standing in contact with KI

META CRESOL.

No.	Cc. Meta cresol	Cc. N 10 Br	Cc. H_2O.	Cc. Conc. HCl.	Time of standing.	Cc. 20% KI.	Cc. Conc. HCl.	Time of standing.	Result.
1	20	50	–	5	1 min.	10	–	1 hr.	97.9
2	20	50	–	5	$^1/_2$ hr.	10	–	2 hrs.	98.48
3	20	50	–	5	1 hr.	10	–	1 hr.	99.2
4	20	50	–	5	$1^1/_2$ hrs	10	–	2 hrs.	99.9
5	20	50	175	5	$^1/_2$ hr.	10	–	2 hrs.	99.6
6	20	50	175	5	$1^1/_2$ hrs.	10	–	2 hrs.	100.07
7	20	50	175	5	3 hrs.	10	–	18 hrs.	99.93
8	20	50	175	5	6 hrs.	40	–	18 hrs.	99.81
9	15	50	175	5	6 hrs.	10	–	5 min.	101.11
10	15	50	175	5	6 hrs.	10	–	$^1/_2$ hr.	100.5
11	15	50	175	5	6 hrs.	10	–	$1^1/_2$ hr.	100.2

No.	cc. Meta cresol.	cc. N/10 I.	g. CH_3COONa $3H_2O$.	g. $NaHCO_3$.	Time of standing.	Procedure.	Result. Per cent.
12	25	40	9		1 hr.	Diluted, added about 5 cc.	118.5
13	25	40	–	0.5	1 hr.	$CHCl_3$ and titrated	122.0
14	25	40	–	2.0	1 hr.	with N/10 thiosul-	130.0
15	25	50	–	2.0	2 hrs.	phate, using starch	155.0
16	25	50	9	–	2 hrs.	indicator.	152.0

(Exps. 1, 2 and 3). If the *m*-cresol solution stands $1^1/_2$ hours in contact with the bromine and then 10 cc. 20 per cent. KI are added and solution is allowed to stand 1 to 2 hours, all the cresol is converted into tribrom-*m*-cresol (Exp. 4).

Dilution permits a more rapid reaction which almost completes itself in $^1/_2$ hour. The addition of KI causes a complete reversal even though the time of standing in contact with free bromine has been much prolonged (Exps. 5, 6, 7, 8, 9, 10 and 11).

It is thus apparent that *m*-cresol may be determined by a conversion into the tribrom compound.

Upon the other hand, when iodine[1] acts upon *m*-cresol in the presence of sodium acetate or sodium bicarbonate, a diïodo compound that may be made the basis of calculation is not produced. More than the theoretical quantity of iodine is absorbed (Exps. 12, 13, 14, 15 and 16).

PARA CRESOL.

No.	Cc. Para cresol.	Cc. N 10 Br.	Cc. H_2O.	Cc. Conc. HCl.	Time of standing.	Cc. 20% KI.	Cc. Conc HCl..	Time of standing.	Result. Per cent.
1	20	50	275	5	1 hr.	10	–	2 hrs.	81.1
2	20	50	275	5	$4^1/_2$ hrs.	10	–	18 hrs.	95.73
3	20	50	–	5	$4^1/_2$ hr.	10	–	18 hrs.	76.35
4	15	50	275	2.5	3 hrs.	10	–	5 min.	97.34
5	15	50	275	5	$1^1/_2$ hrs.	30	–	18 hrs.	89.73
6	10	25	200	2.5	3 hrs.	10	–	18 hrs.	101.8
7	10	25	200	2.5	3 hrs.	20	–	18 hrs.	101.75
8	10	25	200	5 hrs.	3 hrs.	10		18 hrs.	97.7
9	10	25	200	2.5	$8^1/_2$ hrs.	10	–	16 hrs.	104.6
10	10	25	200	2.5	4 hrs.	30	5	20 hrs.	84.94
11	10	25	200	2.5	5 hrs.	30	5	40 hrs.	82.90

No.	cc. Para cresol.	cc. N/10 I.	g. CH_3COONa $3H_2O$.	Time of standing	Procedure.	Result.	cc. Excess.
12	25	30	9	1 hr.	Diluted, added 5 cc.	98.81	25
13	25	30	15	1 hr.	$CHCl_3$, titrated with	99.56	25
14	25	40	9	1 hr.	N/10 thiosulphate,	99.75	25
15	25	50	9	1 hr.	using starch as in-	99.75	25
16	25	50	9	2 hrs	dicator.	99.75	25

[1] "Preparations of Iodo Derivatives of Phenol" (E. Richard), *J. Pharm. Chem.*, **1902**, 15 [5] 217–221. Abstr.—*J. Soc. Chem. Ind.*, **1902**, 423. "New Class of Iodated Phenols" (Messenger and Vortmann), *Ber.*, **22**, 2312–2322. Abstr.—*J. Chem. Soc.*, **1889**, 1150.

Para cresol absorbs bromine much more slowly than either of the other cresols. Under similar experimental conditions, 4½ hours' standing in contact with free bromine results in absorption of only 95.73 per cent. of the theoretical quantity (Exps. 1, 2, and 3). If concentration of free bromine is increased and the usual quantity of HCl decreased one-half, the bromine in combination exceeds the amount necessary for the formation of a dibrom-*p*-cresol brom or tribromcresol compound and 18 hours' standing does not result in sufficient decomposition even though the quantity of KI is doubled (Exps. 4, 5, 6, 7, 8 and 9).

However, an increase in both HCl and KI results in a most pronounced reversal[1] which is due to the decomposition of dibrom-*p*-cresol brom into dibrom-*p*-cresol (Exps. 10 and 11).

Here again the result is directly dependent upon conditions and previous knowledge is necessary on part of the operator.

Now when iodine reacts with *p*-cresol in presence of the condensing agent, sodium acetate, diïodo-*p*-cresol is formed in theoretical quantity if sufficient time is allowed for reaction to complete itself.

This reaction is made the basis of a method for the determination of *p*-cresol (Exps. 12, 13, 14, 15 and 16). The procedure is exactly the same as that given under *o*-cresol.

SUMMARY.

1. Usual bromine methods for determination of cresol depend upon fixed conditions presupposing a previous knowledge on the part of the operator, and while they may be of service they do not satisfy the demand for a desirable method.

2. Tribrom-*o*- and *p*-cresol brom compounds can not be formed in a manner analogous to the production of 2,4,6-tribrom phenol brom. Dibromcresol brom compounds are formed and finally tribromphenol brom; however, *o*- and *p*-cresols can not be determined volumetrically by a conversion into these compounds.

3. Meta cresol is determined by a conversion into tribrom-*m*-cresol.

4. Ortho and para cresols form diïodo compounds, and this reaction is made the basis of a method for their determination.

5. Meta cresol does not yield diïodo compounds under the same conditions; hence, cresol U. S. P. or any mixture containing *m*-cresol can not be determined by a volumetric iodine method.

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[1] "Zur Quantitativen Bestimmung des Phenols und Parakresols in Gemischen derselben und ihre Anwendung auf den Harn," *Pharm. Zentralhalle*, **1911**, 1288.

THE ACCURATE VOLUMETRIC DETERMINATION OF PHOSPHORIC ACID IN PHOSPHATE ROCK.

By JOHN G. FAIRCHILD.

Received January 30, 1912.

The method of determining the phosphoric acid content of phosphate rock here described is a modification of Pemberton's caustic alkali titration, which has the great advantage of being quicker than other volumetric or gravimetric methods. The difficulty experienced in the use of the Pemberton method has been invariably a low result compared with that obtained by the standard method of weighing the phosphoric acid as magnesium pyrophosphate. After close observation of the successive operations whereby the yellow precipitate is dissolved in an excess of standard alkali and this excess titrated after addition of a few drops of phenolphthalein, it was noticed that the final end point was considerably delayed, and this was the more marked the greater the amount of phosphoric acid present or the larger the aliquot parts taken.

In the belief that if this behavior of the indicator toward phosphoric acid could be overcome the method would be very accurate, the suggestion of Sutton[1] was adopted, namely, to precipitate out the phosphoric acid with barium chloride in excess before titrating the excess of alkali. The results stated below show how the method is improved by this modification.

In the first place low results being obtained in dealing with phosphate rocks by standardizing the alkali solution against microcosmic salt in the old way, it was thought possible that the other salts in the rock solution interfered with the titration. A rock solution whose phosphoric acid content was accurately determined gravimetrically was taken as the standard. The average of four results (32.69, 32.82, 32.88 and 32.93) obtained by using different aliquot[2] parts of a 2 gram solution was found to be 32.83 per cent. P_2O_5. Double precipitations were made after weighing the first precipitate, any calcium sulfate or silica being removed by its solution in sulfuric acid with alcohol. The second weights were only 0.1 to 0.3 mg. less, so that this correction could be disregarded.

The next step was to take an aliquot part, preferably 0.1 gram, add 20 cc. of strong ammonia (sp. gr. 0.90), make acid with 1 : 1 nitric acid, and add slowly 25 cc. of warm molybdate solution (about 40° C.). The temperature of formation of the yellow precipitate here is most important, the limits being 45° to 55° C. After shaking for five minutes the precipitate is let stand till cool, then filtered through a 9 cm. No. 590 S. & S. paper and washed, once with a 2 per cent. nitric acid solution and then with a 2 per cent. potassium nitrate solution till the washings cease to redden blue litmus. Paper and precipitate are then transferred to the original flask and dissolved in an excess of standard alkali; diluted slightly with cold water; three drops of phenolphthalein solution are added and one drop of methyl orange (to give a sharper end point). Excess of alkali is then titrated with standard acid, either nitric or hydrochloric. Next, about 8 cc. excess of alkali are again added and 10 cc. of a 10 per cent. solution of neutral $BaCl_2$, which is usually sufficient to precipitate all the phosphate, the molybdate, and also any carbonate. The important feature is the elimination of the phosphate. After again titrating the excess of alkali the two readings show 32.6 cc. and 33.1 cc. The results of several

[1] *Volumetric Analysis*, 9th Ed., p. 113.

[2] Pipettes used were standardized to the flask.

determinations gave this difference of 0.5 cc. Dividing the amount of P_2O_5 present, 0.03283 gram, by 32.6 and by 33.1 gives two values per cubic centimeter, namely, 0.001007 and 0.000992 gram P_2O_5, a difference of 1.5 per cent.

Again, taking the value per cubic centimeter as 0.001007 gram P_2O_5 and multiplying this by 33.1, the correct number of cubic centimeters required for 0.1 gram of the standard rock solution, the percentage of P_2O_5 found is 33.33, which is 0.51 per cent. too high in P_2O_5, or a 1.5 per cent. actual error corrected by the use of $BaCl_2$.

A solution of microcosmic salt was then prepared by dissolving 2.088 grams in some water containing 40 cc. 1 : 1 nitric acid and diluting to 500 cc. Several portions of 25 cc., equivalent theoretically to 0.03546 gram P_2O_5, were taken and their content, determined gravimetrically, was found to be 0.03575 gram P_2O_5. Exactly the same value was found by using 50 cc. of solution. A volumetric determination was now made on 25 cc., which required 35.5 cc. of alkali, barium chloride not being used. Excess of alkali was again added with 10 cc. of $BaCl_2$ and the excess titrated. The result of the second titration was 36.0 cc. Multiplying the value of the alkali solution previously obtained against the standard phosphate rock we have $36.0 \times 0.000992 = 0.03571$ gram P_2O_5 which is the exact amount taken for analysis. If the first burette reading is used we have $35.5 \times 0.000992 = 0.03522$ gram P_2O_5, a difference of 0.5 per cent. of P_2O_5, or 1.5 per cent. actual error, as before.

Although this calculation proves that microcosmic salt can be safely used in standardizing the alkali solution, still, in order to show more strongly that such salts as calcium nitrate have no effect on the titration figure, sufficient pure dry calcium carbonate was added to the nitric acid solution of the microcosmic salt to form tricalcium phosphate with all the phosphoric acid. The same aliquot portions were taken, precipitated, and titrated with these results: without $BaCl_2$, 35.5 cc.; after addition of $BaCl_2$, 36.0 cc. These check the results first obtained.

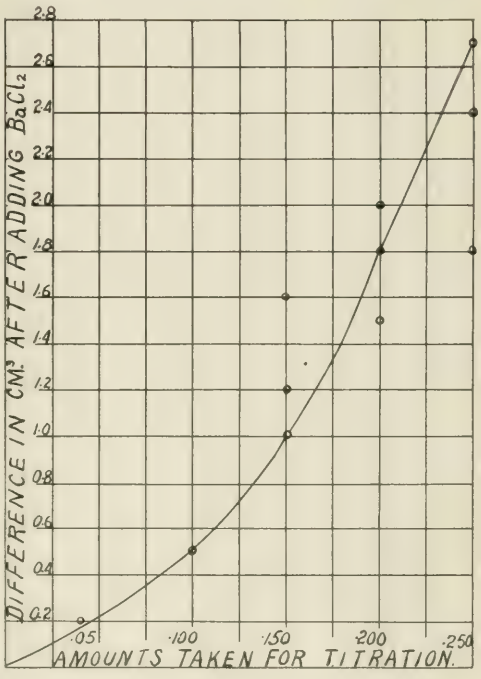
The value of the alkali solution having in this way been fixed very accurately, analyses of a series of eight phosphate rocks (from different localities in order that all probable variations might occur in the composition of the rock solution) were made in the regular way by both volumetric and gravimetric methods. Two grams of the rock powder were put with a little water in a small covered casserole and digested on the steam bath with 40 cc. of 1 : 1 nitric acid for 20 minutes or more. The filtered solution was made up to 200 cc., a portion amounting exactly to 0.1 gram being taken for the volumetric and 0.5 gram for the gravimetric determination. In the preceding table will be found the results of single determinations.

Volumetric, per cent.	Gravimetric, per cent.	Differences.
31.68	31.70	—0 02
25.42	25.74	—0 32
31.79	31.99	—0.20
14.40	14.34	+0.06
24.83	24.67	+0.16
20.66	20.42	+0.24
24.43	24.49	—0 06
37.82	37.93	—0.11
	Sum.	—0 25

Average difference = 0.03 per cent.

Examination was next made of the insoluble residues. Four of these were combined and the papers were ashed in a large platinum crucible and fused with sodium carbonate. Silica was removed by evaporation of the acidified solution in a porcelain dish, the residue taken up with hot 1 : 1 nitric acid, and test made for P_2O_5. Only a trace was found. The papers of the second four were ashed, the silica volatilized with HF and H_2SO_4, the HF being practically all expelled by repeated evaporation on the steam bath. After oxidation with HNO_3, filtration, addition of ammonia and about 10 grams of NH_4NO_3, the P_2O_5 found after dividing by 8 was 0.05 per cent. Several other tests have been made of residues insoluble in hot dilute nitric acid and only once was as much as 0.10 per cent. found, the usual result being no more than a trace.

The curve below shows the effect of $BaCl_2$ on the titration when increasing amounts of phosphate solution are used.



These are the actual percentages:

Portions (gram).....	0.04	0.100	0.150	0.200	0.250
With $BaCl_2$.....	33.02[1]	32.84	32.84	32.84	32.84
Without $BaCl_2$.....	32.50	32.34	32.14	32.14	32.01

The following results compare the two methods just described, the old method of weighing the yellow precipitate direct, and Blair's method[2] of reducing the molybdic acid followed by titration with $KMnO_4$.

[1] Single determination. About 0.2 per cent. high. See curve.

[2] *Analysis of Iron*, 6th Ed., p. 92.

The factor used for P_2O_5 in the ammonium phosphomolybdate was 0.03782. The yellow precipitate was washed well with 2 per cent. nitric acid and dried in a porcelain Gooch crucible at 125° C. to constant weight.

Weighed as ammonium phosphomolybdate.

	Gram.	Per cent P_2O_5.
Portion taken	0.250	32.66
Fresh sample	0.500	32.70

Reduction Method.

Portion taken.

Gram.	Per cent. P_2O_5.
0.025	32.94
0.050	32.94
0.050	32.51
0.050	32.51

Blair's reduction method[1] gives accurate results when extreme care is taken to wash the yellow precipitate entirely free from the molybdate precipitant. Inasmuch as the portion taken here is very small, any slight difference in cubic centimeters of $KMnO_4$ used is multiplied by a large factor four times the factor for the caustic alkali titration. A difference of 0.35 cc. on a 0.05 gram portion gives a difference of 0.40 per cent. in P_2O_5 content.

It is important to bear in mind that the barium phosphate precipitate hydrolyzes rather rapidly, so that the titration should be finished in 15 minutes. If let stand an hour or more the pink color returns to the indicator. The reaction is probably like this:

$$\dot{\dot{B}}a_2(\acute{H}\acute{P}O_4)_2 + 2\dot{H}\acute{O}H \rightleftharpoons \dot{\dot{B}}a(\ddot{O}H)_2 + \dot{\dot{B}}a(\acute{H}_2\acute{P}O_4)_2$$

The phenolphthalein is then affected by the barium hydrate. With precipitates containing more than 0.035 gram P_2O_5 it requires more care in order to strike the true end point. The plan followed above was to close the flask and shake it violently a few minutes, keeping it cold. With smaller precipitates there is no difficulty.

The least amount of molybdate solution necessary to completely precipitate 0.030 gram of P_2O_5 was found to be 20 cc. One cc. of this solution contains 0.048 gram MoO_3 and will precipitate, theoretically, 0.002 gram of P_2O_5. When only 15 cc. were used on a 0.1 gram portion of the standard rock solution 25.5 cc. of alkali were required for solution of the phosphomolybdate. On adding 5 cc. more of molybdate solution to the filtrate and titrating the precipitate, 7.2 cc. more of alkali were used, a total of 32.7 cc., whereas the correct figure was 33.1 cc. To insure a noticeable excess 25 cc. of the molybdate solution are added.

By allowing 20 minutes for solution of the rock the time for a single determination will average not more than one hour.

As a final test, the amount of error due to expansion of the standard solutions was fixed. A standard alkali solution was transferred to a 100 cc. flask up to the mark and its temperature taken. The solution was then heated exactly 10° and the rise in volume noted on the neck of the flask. This increment was then withdrawn by a pipette and its value found by running in from a burette enough to reach the top mark again. This difference due to 10° C. was found to be 0.2 cc., an error altogether negligible.

[1] Factor MoO_3: Fe, 0.85714.

In conclusion, it is seen that the greatest accuracy possible by the gravimetric method is 0.50 per cent., or 0.15 per cent. of the P_2O_5 content, and it varies to 0.75 per cent., or 0.25 per cent. P_2O_5. The accuracy of the caustic alkali method is a trifle over 1 per cent. actual error, or a difference of 0.30 per cent. P_2O_5 in the rock.

STANDARD SOLUTIONS.

Caustic Alkali.—31 grams of the C. P. soda sticks dissolved in water and diluted to 2 liters: 1 cc. equals about 0.001 gram P_2O_5. The small amount of CO_2 present, about 0.12 per cent., is negligible.

Nitric Acid.—Practically a 2 per cent. solution which is diluted till 1 cc. equals 1 cc. alkali solution.

Phenolphthalein.—A 1 per cent. alcoholic solution.

Methyl Orange.—A 0.1 per cent. solution.

Molybdate Solution.—100 grams MoO_3, 144 cc. NH_4OH (sp. gr. 0.90), and 271 cc. H_2O; 489 cc. HNO_3 (sp. gr. 1.42) and 1.148 cc. H_2O.

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THE DETERMINATION OF TOTAL MANGANESE IN SOILS.

By Ross A. Gortner and Clayton O. Rost.

Received January 25, 1912.

INTRODUCTION.

It is a well-known fact that the gravimetric estimation of small quantities of manganese, such as occur in rocks or soils, is highly inaccurate even when great care is used. The inaccuracy may be caused by a number of factors, including incomplete separation from the iron and aluminium, incomplete precipitation, and contamination of the precipitate by other substances. These errors, because of the small amounts of manganese present, can not be depended on to balance each other.[1] The usual method which is now employed is to determine the manganese colorimetrically after oxidation to permanganic acid. Various means of effecting this oxidation have been employed. The oldest method is the oxidation of the manganese in nitric acid solution by the addition of lead peroxide.[2] This material proved unsatisfactory owing to the necessity for the removal of the excess of the lead peroxide, which settled very slowly.

Acting on the suggestion of Marshall,[3] Walters[4] substituted ammonium persulfate for the lead peroxide. All of Walters' determinations were made either on steel, pig irons or blast furnace cinders. This method was later adopted by Hillebrand[5] and Washington[6] for the determination of total manganese in rocks.

Essentially the method consists in decomposing the rock powder in a platinum basin by means of hydrofluoric and sulfuric acids, expelling the excess of hydrofluoric acid by repeated evaporation with small amounts of sulfuric acid, evaporating almost to dryness, diluting with 1 : 1 nitric acid, filtering, and

[1] See Hillebrand, *Bull.* **422**, 116, U. S. Geol. Survey.
[2] Pichard, *C. R. acad. sci.*, Dec. 30, 1872.
[3] Marshall, *Chem. News*, **83**, 76 (1901).
[4] Walters, *Ibid.*, **84**, 239 (1901).
[5] *Loc. cit.*
[6] Washington, "The Chemical Analysis of Rocks," Wiley and Sons, N. Y., 1910.

oxidizing the manganese to permanganic acid by the addition of ammonium persulfate. The permanganic acid solution is then diluted to a known volume and the color read against a solution of known strength in a colorimeter.

In applying this method to Nebraska soils, following the detailed directions of Washington[1] we have found that in many cases we could not obtain concordant results on duplicate determinations, the variation between duplicates being sometimes as much as two hundred per cent. Brinton[2] has already noted that in some iron ores the treatment with sulfuric and hydrofluoric acids does not give complete extraction of the manganese, and we have found that this is the case with all of the soils which we have investigated. In most of these soils, three, and in some cases four, extractions with hydrofluoric and sulphuric acids were necessary before all of the manganese was obtained in solution. Inasmuch as each extraction requires nearly three hours, it will be seen that to accurately determine manganese in soils by this method is a very tedious operation. We have, therefore, endeavored to devise a method which is much more rapid, more accurate, requires less attention, and eliminates all fumes of hydrofluoric acid or sulfur trioxide. The smaller amount of platinum required in the process is also a decided advantage.

As an oxidizer we have used sodium bismuthate instead of ammonium persulfate, inasmuch as it gives a better oxidation, always giving the true permanganate color while the persulfate oxidation often produces a reddish tint that is difficult to read accurately. Blair[3] and Brinton[4] seem to recognize the superiority of the "bismuthate" oxidation by stating that "for samples containing not over 2 per cent. of manganese the bismuthate is the most accurate method known." Walters[4] states that the persulfate oxidation does not always progress smoothly for when the salt is dry "the reaction is very incomplete and irregular and not to be depended on", a fact that is not mentioned in the description of the method by Hillebrand or Washington. By moistening the persulfate much more concordant results are obtained, but we have found that the bismuthate is much more reliable than the persulfate. In some instances we were unable to oxidize all of the manganese by means of ammonium persulfate but when these same solutions were reduced with sulfurous acid and reoxidized with bismuthate the correct percentage of manganese was obtained. The bismuthate method has the added advantage over the persulfate in that it is not necessary to add silver nitrate to catalyze the reaction.

EXPERIMENTAL.

The Estimation of Manganese in Soils by Walters' Method.—The soil, which had been ground to pass through bolting cloth of 0.1 mm. mesh, was treated with hydrofluoric and sulfuric acids as described by Washington[1] and the manganese determined in the extract. The first part of Table 1 shows the results which were obtained on eight different soils. Soil number 3490 was selected to determine whether or not all of the manganese was rendered soluble with one extraction, and it was found that in some instances four extractions were necessary to completely remove all traces of manganese. In those samples where several extractions were made, the total amount of manganese obtained was nearly a constant, but even in these there is too great an error for exact work, for, although the maximum difference between duplicates is only 0.010 per cent., this error represents almost ten per cent. of the total manganese present.

The Estimation of Manganese in Soils by our Method.—One gram of soil is intimately mixed with four grams of manganese-free, dry, sodium carbonate and fused in a 20 cc. platinum crucible over a blast lamp until the melt is quiet, usually after about ten minutes' fusion. The liquid mass is then poured into a platinum basin and the basin rotated in order to obtain the melt in a thin film, thus providing for more rapid solution. The melt and the crucible are then treated with about 100 cc. of distilled water and heated on a water bath in either a platinum or a porcelain dish[2] until the fused product is completely disintegrated. The crucible is then removed from the dish, any adhering solution washed off, and the mixture acidified with 130 cc. of 35 per cent. (by weight) sulfuric acid[3] and diluted to 250 cc. Should there be a heavy precipitate of silica at this point it is advisable to filter, using a Büchner funnel and filtering by suction. This is seldom necessary, however, for in most cases the silica does not precipitate to any extent, but merely produce a slight opalescence which does not interfere with the permanganate readings. One hundred cc. of this solution are then placed in a beaker and from 0.25 gram to 1 gram of sodium bismuthate added, depending on the quantity of manganese present. We have found that 0.25 gram is sufficient where the manganese content does not exceed 0.20 per cent. The oxidation mixture is then heated to boiling and the boiling continued until the liquid has the true permanganate tint. If there is any red coloration the boiling has not been continued long enough. The solution is then cooled and read in a colorimeter or Nessler's glasses against a standard solution of permanganic acid which has been prepared by reducing a solution of potassium permanganate in 20 per cent. sulfuric acid by the cautious addition of sulfurous acid, and reoxidizing with bismuthate. This standard solution should contain about 0.2 mg. of MnO per 10 cc. From the ratios thus obtained the quantity of manganese in the original sample

[1] *Loc. cit.*

[2] Brinton, THIS JOURNAL, **3**, 237 (1911).

[3] Blair, *J. Am. Chem. Soc.*, **26**, 793; also *Chem. Anal. of Iron*, 7th Ed. p. 121.

[4] *Loc. cit.*

[1] *Loc. cit.*

[2] Glass should not be used inasmuch as the alkali might attack the glass and dissolve out some of the manganese which is present in most laboratory glass, including Jena apparatus. See Gortner, *Am. Chem. J.*, **39**, 157 (1908).

[3] This excess of sulfuric acid is employed inasmuch as the oxidation progresses more rapidly and basic bismuth salts do not precipitate. The same results may be obtained when half of this quantity of acid is used, but the oxidation requires several minutes' boiling and the permanganic acid solution must be filtered through asbestos in order to free the solution from precipitated bismuth salts.

is calculated. After a little practice, the complete operation can be carried out in an hour and a half, so that in this respect alone the method is greatly to be preferred.

When duplicate determinations are desired only one fusion is necessary, for two separate oxidations may be taken from the total 250 cc. In the data which are given in the last column of Table 1 each figure represents a separate fusion and oxidation, and in the sixteen determinations, representing duplicate fusions on eight different soils, the maximum difference between duplicates amount to only 0.002 per cent. No determinations were discarded in compiling this table.

TABLE 1.—PERCENTAGE OF MnO FOUND BY WALTERS' METHOD AS DESCRIBED BY WASHINGTON, AND BY OUR NEW METHOD.

Exp No	Soil No	Walters' method, MnO in extractions I-IV. I.	II	III.	IV.	Total	Authors' method
1	3490	0.082	0.020	0.004	trace	0.106	0.109
2	3490	0.080	0.027	0.005	?	0.112	0.111
3	3490	0.060	0.042	trace	?	0.102	
4	3490	0.095	0.013	trace	?	0.108	
5	3490	0.095	0.013	trace	?	0.108	
6	3490	0.064	0.016	not			
7	3490	0.046	0.029	determined			
8	3486	0.045	not determined				0.107
9	3486	0.052					0.105
10	3487	0.018					0.111
11	3487	0.028					0.110
12	3488	0.020					0.111
13	3488						0.112
14	3489	0.025					0.120
15	3489	0.031					0.119
16	3491	0.044					0.123
17	3491	0.044					0.125
18	3483	0.060					0.096
19	3483	0.060					0.098
20	3459	0.033					0.067
21	3459						0.067

SUMMARY.

1. We have found that Walters' method for the determination of small quantities of manganese, as described by Washington and Hillebrand, is not applicable to Nebrasks soils, but that in some instances four extractions on a one-gram sample with hydrofluoric and sulfuric acids were necessary before all of the manganese was obtained in solution.

2. We have found that when such soils are fused with sodium carbonate and the solution of this melt is acidified with sulfuric acid and oxidized by means of sodium bismuthate, that all of the manganese is oxidized to permanganic acid, and may easily be estimated colorimetrically.

3. We claim for this method greater rapidity, absence from irritating fumes, less danger of loss by spattering, more ease of operation in unexperienced hands, duplicate determinations on one sample of soil, and much greater accuracy.

ALTERING THE COMPOSITION OF INDIAN CORN BY SEED SELECTION.[1]

By L. H. SMITH.

Received January 8, 1912.

In a paper presented before the American Chemical Society in 1899 Dr. C. G. Hopkins reported a line of experiments undertaken at the Illinois Experiment Station to influence the composition of the corn kernel by selection and breeding. At that time the experiments had been under way only about two years, but already results had been obtained sufficiently pronounced to indicate the possibility of changing the composition of the corn kernel as regards protein, oil and carbohydrates. In fact, in his conclusion the author remarks that "while it may require ten or twenty years' work to enable one to form a very definite opinion as to the extent to which it is possible to influence the chemical composition of corn, it is believed that the data thus far obtained may be of practical and scientific value."

Since the time this statement was made this investigation has been continued and twelve years' work has been added to these experiments. No further report, however, has been given to this Society, and in view of this fact it was thought that the members would be interested to learn regarding the present status of the work.

Inasmuch as the general purpose of the investigation and the methods of carrying it out have been given already quite fully in the above-mentioned paper and elsewhere (see *Bull.* **128,** Illinois Agricultural Experiment Station), it will be the present plan to mention only as much of this matter as is necessary to an intelligent understanding of the results, the chief purpose being to give a brief résumé of the results up-to-date.

Stated briefly, the proposition involved in this investigation was to take a variety of corn and through selection and breeding try to influence the composition of the grain in four different directions, namely: 1, Increase the protein content; 2, Decrease the protein content; 3, Increase the oil content; 4, Decrease the oil content.

Through a preliminary study involving the analyses of a good many samples of different ears and parts of ears the principles of the selection were established. It was found that there is considerable variation among different ears with respect to composition, while the kernels within a single ear are comparatively uniform; that is to say, the ear can be taken as the unit of selection and this gives the working basis. Thus the method is to take two or three rows of kernels lengthwise of the ear as a sample for analysis. If the ear proves to be suitable for seed the remaining kernels are planted.

Starting in 1896 with a variety then known as Burr's White, 163 ears were chosen and analyzed, determinations being made for protein, oil, ash and carbohydrates. According to the percentage of the constituents, four lots of these ears were picked out with which to start the four respective breeding plots, a high protein plot, a low protein plot, a high oil plot, and a low oil plot. Each ear was planted in a separate row, the different plots being isolated in order to avoid contamination from cross pollination. From the harvest a large number of ears were analyzed from each plot, and based upon these results ears were selected for seed with which to plant the respective plots the following year.

This general plan, with a few minor changes of

[1] Presented at A. C. S. Meeting at Washington, D. C., December, 1911.

detail, has been followed year after year until we now have the results for 14 generations (the samples for the fifteenth generation have not yet been analyzed). In this manner four different strains emanating from the same variety have been derived. It has been extremely interesting to watch their gradual evolution. This may be shown in outline by the following tabular arrangement:

BREEDING FOR HIGH AND LOW PROTEIN.

Average per cent. protein in crop each generation.

Year.	High protein.	Low protein.	Difference.
1896	10.92	10.92	0.00
1897	11.10	10.55	0.55
1898	11.05	10.55	0.50
1899	11.46	9.86	1.60
1900	12.32	9.34	2.98
1901	14.12	10.04	4.08
1902	12.34	8.22	4.12
1903	13.04	8.62	4.42
1904	15.03	9.27	5.76
1905	14.72	8.57	6.15
1906	14.26	8.64	5.62
1907	13.89	7.32	6.57
1908	13.94	8.96	4.98
1909	13.41	7.65	5.76
1910	14.87	8.25	6.62

BREEDING FOR HIGH AND LOW OIL.

Average per cent. oil in crop each generation.

Year.	High oil.	Low oil.	Difference.
1896	4.70	4.70	0.00
1897	4.73	4.06	0.67
1898	5.15	3.99	1.16
1899	5.64	3.82	1.82
1900	6.12	3.57	2.55
1901	6.09	3.43	2.66
1902	6.41	3.02	3.39
1903	6.50	2.97	3.53
1904	6.97	2.89	4.08
1905	7.29	2.58	4.71
1906	7.37	2.66	4.71
1907	7.43	2.59	4.84
1908	7.19	2.39	4.80
1909	7.05	2.35	4.70
1910	7.72	2.11	5.61

In considering these data attention should be called to the fact that environmental conditions exert an influence upon the protein as well as the oil content and a study of these results reveals some pronounced seasonal effects. By having a "high" and a "low" plot of each, however, we obtain a check which enables us to eliminate these seasonal effects to some extent. Thus the last column of the table showing the difference in per cent. each year furnishes the best information of the real progress due to heredity.

Without going further into a detailed discussion of the figures we may say by way of summary that starting with a variety of corn of average composition it has been possible by 14 years of breeding to increase the protein content from 10.92 per cent. in the original, to 14.87 per cent. in the crop of 1910, at the same time by selection in the opposite direction, to decrease this constituent to 8.25 per cent. Even more striking changes than these have been produced in the oil content. The oil has been increased from 4.70 per cent. in the original to 7.72 per cent in the crop of 1910 while at the same time in another strain it has been decreased to 2.11 per cent.

In other words, out of a single variety of corn two strains have been developed of which one is now nearly twice as rich in protein as the other, and two other strains have been developed, the one of which is now more than three times as rich in oil as the other.

The question arises as to the effect of this selection upon the composition of parts of the plant outside of the kernel. This matter has been studied by analyzing each year different plant parts in the various strains. Without entering into any discussion of the results it may be stated in a general way that as yet we have been able to find no pronounced changes in the composition of other parts of the plant resulting from the changes produced in the grain.

Another practical question always arises in this connection, and that is regarding the effect of this selection upon productive qualities. It may be said that in spite of the rigorous selection for special characters to which this corn has been subjected, the yields in these four strains have, in general, been quite well maintained. Selection for high protein seems to have been accompanied in this instance by a somewhat diminished yield as measured by bushels of corn per acre. If, however, we place it upon the basis of pounds of protein per acre our high protein strain is sufficiently higher in percentage, so that it yields more protein per acre than the ordinary varieties growing alongside it in the productivity tests.

COLLEGE OF AGRICULTURE,
UNIVERSITY OF ILLINOIS.

RELATION OF ACTIVE POTASH TO POT EXPERIMENTS.[1]

By G. S. FRAPS.

Received March 25, 1912.

By the term "active potash" we mean that soluble in $N/5$ nitric acid. This solvent has been in use for some time for extracting the more soluble potash and phosphoric acid from the soil. As pointed out in a previous article, the quantity of phosphoric acid extracted is related to the results of pot experiments on the soil. Similar experiments will here be reported on potash.

Pot experiments with representative Texas soils have been made at this station for seven years. The experiments have been carried on under diverse conditions, sometimes not favorable to the best growth of the plants. The plants were grown in Wagner pots containing 500 grams soil, applications of fertilizer being made to the various pots. The pots were kept in houses covered partly or completely with canvas, in order to moderate the temperature. A crop is regarded as very deficient if it is only 50 per cent. or less, of the completely fertilized crop. If less than 90 per cent., it is considered deficient (D). If between 90 and 110 per cent., it is considered as not deficient (S). If over 110 per cent., it is considered that the fertilizer injures the crop (T). The crop without potash (PN) is always compared with the crop with potash (PNK).

Relation of Deficiency to Active Potash.—The 172 soils studied have been divided into groups according to their content of active potash. The following

[1] A full account of this work will be published as *Bulletin* **145** of the Texas Experiment Station.

table shows the percentages of deficient crops, D and DD, and of those injured by potash T.

The percentage of deficient crops decreases with the quantity of active potash in the soil. The percentage of injured crops increases with the quantity of active potash in the soil.

TABLE I.—RELATION OF ACTIVE POTASH TO NUMBER OF DEFICIENT CROPS.

Active potash in soil Parts per million.	Percentage deficient. (DD and D).	Percentage injured. (T).
0–50	86.7	7
50–100	58.1	17
100–150	54.3	16
150–200	39.1	17
200–300	37.5	31
300–400	42.6	28
400–600	15.0	46
600–800	18.0	44

Relation to Weight of Crop.—The weight of the crop without potash divided by the weight with potash, expressed in percentages, shows the relative effect of the potash on the growth of the plant. The average figures for 403 crops are given in Table II.

TABLE II.—RELATIVE SIZE OF CROP WITHOUT AND WITH POTASH.

Active potash in soil in parts per million.	Percentage PN/PNK.
0–50	67
50–100	79
100–150	84
150–200	91
200–300	100
300–400	98
400–600	101
600–800	116

The effect of fertilizer potash on the weight of the crop decreases with the active potash in the soil. When the active potash exceeds 200 parts per million, the fertilizer potash effects no increase, on an average.

Relation to Potash Content of Crop.—The average potash content of (*a*) the corn crop and (*b*) the kaffir and sorghum crop, is given in Table III.

TABLE III.—RELATION OF ACTIVE POTASH OF SOIL TO POTASH CONTENT OF CROP.

Active potash in parts per million.	Percentage of potash.	
	Corn crop.	Kaffir and sorghum crop.
0–50	1.38	0.78
50–100	1.70	0.93
100–150	2.29	0.89
150–200	2.55	1.45
200–300	3.65	1.68
300–400	3.53	1.72
400–600	3.83	2.44
600–800	4.31	1.79

The potash content of the crops increases with the active potash content of the soil.

Relation of Active Potash to Total Potash Removed.—The average and maximum quantity of potash removed by the crop which received no potash is given in Table IV.

TABLE IV.—RELATION OF QUANTITY OF POTASH REMOVED BY ALL CROPS TO ACTIVE POTASH OF SOILS.

Potash in soil. Parts per million.	Potash removed by crops in parts per million of soil.	
	Average.	Maximum.
0–50	29.3	53.4
50–100	37.2	143.3
100–150	51.0	176.2
150–200	80.9	249.6
200–300	120.1	434.6
300–400	156.9	354.8
400–600	119.4	295.8
600–800	206.9	380.8

The average quantity of potash removed by the crop increases with the active potash content of the soil.

SUMMARY AND CONCLUSIONS.

1. The average percentage of crops deficient in potash decreases with the active potash in the soil.

2. The average percentage of crops injured by potash increases with the active potash in the soil.

3. The effect of fertilizer potash on the weight of the crop decreases as the active potash content of the soil increases.

4. The percentage of potash in the crop increases as the active potash in the soil increases.

5. The total potash removed by the crop from the soil increases as the active potash content of the soil increases.

AGRICULTURAL EXPERIMENT STATION,
COLLEGE STATION, TEXAS.

THE DETECTION OF FORMIC ACID IN FRUIT PRODUCTS.

By F. L. SHANNON.

Received March 22, 1912.

In *Bull.* **195,** of the Dairy and Food Department of the State of Michigan, the author called attention to the fact that formic acid was being used in this country as a preservative of fruit products.

It has been the general belief among chemists, for some time, that some preservatives other than the ones ordinarily found were being used in the preservation of fruit products, and investigations have been made in various laboratories throughout the country for the purpose of determining the identity of the substance used. Owing to its use in Germany, a number have suspected formic acid and have built up their investigations with that substance in mind, but because of the unsatisfactory and indirect methods of identification it has been difficult to reach a positive conclusion.

A search of the literature on the subject revealed the fact that the detection of formic acid did not depend upon its isolation and subsequent identification, but mainly upon the indirect method of its reducing power, principally upon silver nitrate and mercuric chloride solution. For example, the older literature states that formic acid is a constant constituent of many plant and animal products, a statement based on the fact that when they are subjected to steam distillation some substance is obtained in the distillate which reduces silver nitrate and mercuric chloride solution. However, in view of recent investigations along this line, it seems that this whole subject of the natural occurrence of formic acid needs further study, as it has been found possible to subject a host of substances which were known to contain no formic acid, to steam distillation and obtain a distillate which gave a pronounced reduction with both silver nitrate and mercuric chloride solution. From none of these substances, however, has it been possible to isolate and identify formic acid as such. Therefore, it is evident that we are not justified in designating as formic acid every substance obtained by steam dis-

tillation which reduces silver nitrate and mercuric chloride solution. It was found, for example, that when phosphoric acid was subjected to distillation, the distillate possessed the reducing properties generally ascribed to formic acid. Furthermore, in a number of methods in which the formic acid recovered by steam distillation is neutralized using phenolphthalein as indicator, the indicator itself was found to have a reducing action on mercuric chloride.

One of the most satisfactory indirect methods for the detection of formic acid is based on its reduction to formaldehyde by means of magnesium and dilute sulphuric acid. Fenton[1] has shown that carbonic acid may be reduced in the same way, but Bacon[2] has called attention to the fact that this is of theoretical importance only, there being no danger of confusing the two in practice. However, every step in this method must be carried out with absolute precision, or erroneous conclusions may be drawn.

The qualitative method as applied to the products used in this investigation is as follows: To about 200–500 cc. of the syrup or crushed fruit in a two-liter, long-necked round bottom flask provided with a Reitmeier bulb, add about 50–100 cc. of water. Subject to steam distillation, collecting the distillate (usually about 2500 cc.) until it ceases to give an acid reaction with litmus. Exactly neutralize the distillate with $N/1$ NaOH, using litmus as an indicator. Evaporate on a steam or water bath to about 50 cc., transferring from the large evaporating dish to smaller ones as the volume decreases. Transfer to an Erlenmeyer flask, provided with a glass tube about three feet long as an air condenser, add a few pieces of pure magnesium ribbon or wire and a slight excess of dilute sulphuric acid and set in a cool place for one hour, adding dilute sulphuric acid through the tube from time to time as the reaction ceases. Transfer the liquid to a suitable distilling flask and collect the first ten cc. of the distillate, which will contain most of the formaldehyde, if the original syrup contained formic acid.

There are a number of methods published for the detection of formaldehyde and nearly every analyst has his favorite test. However, the methods which proved the most satisfactory in this work were, Leach's Method,[3] Phloroglucinol Method,[3] Rimini's Method,[3] and the Rescorcin Method of the United States Pharmacopoeia. A positive reaction with *these four tests* was considered conclusive evidence of the presence of formaldehyde.

CRYSTALLOGRAPHIC IDENTIFICATION.

Inasmuch as practically all methods for the detection of formic acid previously reported are indirect methods depending upon the decomposition of the formic acid or upon its reducing powers, it seemed desirable to attempt the isolation of formic acid in the form of an insoluble salt.

The usual procedure in determining the identity of an organic acid in plants is to prepare some readily crystallizable salt, sparingly soluble in water. Of the various formates the lead salt crystallizes readily without water of crystallization, is very stable and requires 63 parts of water for solution. The formation and identification of lead formate would therefore constitute a direct and positive proof of the presence of formic acid. After numerous attempts the following procedure was adopted:

Steam distil about 1000–1200 cc. of the syrup as in the first operation, collecting the distillate (2500–3000 cc.) in a receiving flask to which about 5 cc. of lead cream has been added. (This is made as follows: Precipitate a solution of lead nitrate with potassium or sodium hydrate in the presence of phenolphthalein until a faint pink color appears. Wash by decantation 8–10 times.) Shake the flask occasionally and as the lead hydrate is dissolved add a few cc. more, until all of the formic acid is combined. Concentrate the liquid in a large dish on a steam or water bath to about 50 cc. Filter and transfer to a suitable crystallizing dish and set aside in a desiccator. If formic acid was present in the original material, needle-like crystals of lead formate will form. Wash the crystals with absolute alcohol, to remove any lead acetate which may be present, spread on filter paper and dry. To the dry crystals apply the following tests:

(*a*) Aqueous solution will reduce $AgNO_3$ upon warming.

(*b*) Aqueous solution will reduce mercuric chloride solution upon warming.

(*c*) Aqueous solution will reduce platinum chloride upon warming.

(*d*) To a portion of the crystals in a dry test tube add sulphuric acid and warm. Carbon monoxide is generated which will burn in the tube with a blue flame when ignited. Further note that the lead formate is not discolored.

(*e*) Transfer some of the crystals to a small distilling flask, treat with concentrated phosphoric acid and distil. The distillate, which is formic acid, will react as follows:

1. Acid to litmus and acid taste.
2. Reduces silver nitrate on warming.
3. Reduces mercuric chloride on warming.
4. Reduces platinum chloride on warming.
5. Is reduced to formaldehyde by magnesium and dilute sulphuric acid.

As previously mentioned it was found that when phosphoric acid and water alone were distilled, the distillate would reduce silver nitrate and mercuric chloride solution. Therefore, before test (*e*) was carried out the phosphoric acid was subjected to distillation until it no longer gave a distillate that would reduce silver nitrate or mercuric chloride. The crystals of the lead compound were then added and the distillation continued.

Although the chemical evidence that the volatile acid obtained from the fruit products used in this investigation is conclusive, it was thought desirable to submit the crystals to Dr. Edward H. Kraus, Professor of Geology and Mineralogy, University of Michigan and he reports as follows:

[1] *J. Chem. Soc. London*, **1907**, 91, 687.
[2] *Circ.* **74**, U. S. Dept. Agric., Bur. of Chem.
[3] *Bull.* **107**, 185, U. S. Dept. Agric., Bur. of Chem.

"The crystals, which were examined crystallographically, were obtained by slow crystallization from an aqueous solution of the material furnished by Percy L. Shannon, State Analyst, Lansing, Michigan. They are prismatic in habit and about 2–3 mm in length and of slightly yellowish color. All crystals were clear and transparent. Although the crystals were in general doubly terminated, readings were made only upon the faces of the prism zone, the end faces being extremely small and, hence, difficult of adjustment. The images obtained were very good, considering the size of the crystals.

"The measured angles, compared with the values given by Plathan,[1] for lead formate are as follows:

			Kraus	Plathan.
m	*m*	(110) (1$\bar{1}$0)	73° 26′	73° 28′
m	*m*	(110) (1$\bar{1}$0)	53° 17½′	53° 16′

"This comparison shows that the agreement in the values for this material and those given by Plathan for lead formate are exceedingly close.

"Parallel extinction was observed upon all the faces examined. The indices of refraction are higher than that of methylene iodide, as determined by the Becke and the Schroeder van der Kolk methods.

"The above crystallographic-optical properties, together with the fact that a distinct reaction for lead is easily obtained upon the plaster tablet with the blowpipe, indicates conclusively that the substance examined is lead formate."

To further substantiate the proof a number of fruit syrups that were known to contain no added formic acid were subjected to steam distillation, and an attempt made to separate a lead compound. In some instances a few crystals were obtained, but at no time would the crystals give the characteristic tests for lead formate.

It would seem then that the formation of formaldehyde coupled with the formation of lead formate and their subsequent identification would furnish a conclusive and positive proof of the presence of formic acid.

The author desires to take this opportunity to thank Dr. Edward H. Kraus for his coöperation in this work.

MICHIGAN DAIRY AND FOOD DEPARTMENT,
LANSING.

[1] Groth, *Chemische Krystallographie*, **1910**, 3, 16.

THE DETECTION OF PRUSSIAN BLUE IN TEA.

By FRED WEST.

Received January 26, 1912.

In this test advantage is taken of the well known blue color reaction between Prussian blue and a solution of oxalic acid.

Grind about 15 grams of the tea to be examined, in a mortar, and pass through a 20-mesh sieve, neglecting the few stems which resist comminution.

Procure five squares of plate glass 15 × 15 cm. each; upon each plate place an 11 cm. circular filter, as thin as procurable and having a smooth surface.

Saturate each filter with test solution oxalic acid, U. S. P., removing any air spaces under filter.

The well wetted filters are now to be sprinkled with the ground tea. This is best performed by sifting the tea from the sieve, holding it about 30 cm. above the plates, which should lie flat. Sprinkle filters well but avoid overlapping the particles of tea.

Allow the filters to dry on the plates in the air. When thoroughly dry remove filters from plates and brush off tea with a stiff brush.

The presence of Prussian blue is indicated by bright blue spots, best seen with the aid of a hand glass, and where large particles of the Prussian blue have rested, the color radiates and spreads through the filter fiber.

If smooth filters are not procurable, rough ones may be used, but a second glass plate should be clamped over the filter to press the particles of tea against the fiber. This necessitates the use of gentle heat to dry the plate.

Comparison of the amount of color in different samples may be observed by noting the total number of spots to each sample, using five plates to each one. Difficulty in counting spots on the filters can be overcome by using a Wolffhuegel counting plate and a large hand lens.

As the natural coloring matter in tea does not stain the filters in the presence of the oxalic acid, this gives a clear white field upon which any blue spots will show very clearly. The blue spots on the filters are fairly permanent and the filters may be attached to the report sheets for reference.

SAN FRANCISCO, CAL.

LABORATORY AND PLANT

FACTORS DETERMINING THE CAPACITY OF A FILTER PRESS.

By C. ALMY, JR., AND W. K. LEWIS.

Received March 18, 1912.

Very little information can be found in the literature regarding the flow of a liquid through a filter cake. Hitherto the popular assumption has been that the rate of flow is, up to a certain point, directly proportional to the pressure and inversely proportional to the thickness of the cake. The object of this investigation has been to establish more accurately the relationships existing between the rate of flow, pressure, and thickness of cake: relationships which, as will be shown, can for any particular sludge be expressed by a simple mathematical equation.

For this purpose we used a chromium hydrate sludge made by reducing dichromate with glucose and precipitating with sodium carbonate. The filter press was a six inch corner-feed laboratory press. It was of course impracticable to measure the thickness of the cake during the progress of a run, but as the volume of filtrate at any time is obviously proportional to the thickness and is an equally significant value in filtration, this figure has been substituted throughout this work in both plots and equations.

Six runs were made, at 100 lbs., 75 lbs., 50 lbs., 25 lbs., 10 lbs. and 5 lbs. pressure per square inch re-

TABLE I.[1]

100 lbs.

Time.	Vol. of filt. Cc.	Time.	Vol. of filt. Cc.
1′ 15″	600	14′ 30″	2400
2′ 55″	1000	18′ 20″	2700
6′ 00″	1500	22′ 35″	3000
8′ 20″	1800	27′ 30″	3300
11′ 15″	2100	32′ 50″	3600

TABLE II.

75 lbs.

Time	Vol. of filt. Cc.	Time.	Vol. of filt Cc.
2′ 15″	800	15′ 35″	2300
4′ 00″	1100	19′ 40″	2600
6′ 10″	1400	24′ 25″	2900
8′ 45″	1700	29′ 30″	3200
11′ 55″	2000	35′ 30″	3500

TABLE III.

50 lbs.

Time.	Vol. of filt Cc.	Time.	Vol. of filt. Cc.
45″	400	16′ 00″	2200
2′ 00″	700	20′ 25″	2500
3′ 45″	1000	25′ 20″	2800
6′ 00″	1300	30′ 50″	3100
8′ 50″	1600	37′ 05″	3400
12′ 10″	1900	42′ 35″	3600

TABLE IV.

25 lbs

Time	Vol. of filt Cc.	Time.	Vol. of filt Cc.
40″	300	17′ 40″	2100
2′ 00″	600	22′ 35″	2400
3′ 55″	900	28′ 10″	2700
6′ 30″	1200	34′ 25″	3000
9′ 40″	1500	41′ 35″	3300
13′ 20″	1800	49′ 05″	3575

TABLE V.

10 lbs.

Time.	Vol. of filt. Cc.	Time.	Vol. of filt. Cc.
2′ 05″	500	21′ 10″	2000
7′ 35″	1100	27′ 10″	2300
11′ 20″	1400	34′ 10″	2600
15′ 55″	1700	42′ 30″	2900

TABLE VI.

5 lbs.

Time.	Vol. of filt. Cc.	Time.	Vol. of filt Cc.
1′ 50″	400	20′ 45″	1800
5′ 20″	800	27′ 25″	2100
10′ 10″	1200	35′ 25″	2400
14′ 55″	1500	41′ 55″	2600

spectively. Two half-inch distance frames were used giving two cakes $^5/_8$″ thick with an area of about 35 sq. in. These runs were all made on the same day with the same sludge, experience having shown us that in order to get comparable results this is absolutely essential. It is impossible to exactly duplicate conditions on two different days, and furthermore the character of the sludge itself has unquestionably been shown to alter very materially on standing.

The sludge which was kept thoroughly agitated was pumped into the frames by hand, and the time recorded for every 100 cc. of filtrate (see Tables I–VI).

From the data in these tables, the six curves in figure 1 were plotted. By means of these curves, the rate of flow was graphically determined at frequent intervals and plotted against the volume of filtrate as before. It is evident that the rate of flow is, as expected, some function of both the volume of filtrate and the pressure. With the object of ascertaining whether the rate was a power function of the volume of filtrate, in which case the relationship could be expressed by the equation,

$$R = f\,\frac{P}{V^n},$$

the logarithms from these curves were plotted as shown in figure 2.[1] It will be seen that with the exception of the 100 lb. run, these are all parallel straight lines for the greater part of their length, showing that up to the break, the rate of flow for a constant pressure is a power function of the volume of filtrate or thickness of cake.

The unexpectedly quick rate of flow for the first part of the 100 lb. run is a phenomenon that was always observed at high pressure and is difficult to satisfactorily account for. Presumably it is due to the fact that the sludge, rushing into the frames with increased velocity, does not at first pack evenly over the surface of the filter cloths but forms small channels through which the liquid flows more readily. It should be mentioned incidentally that a pressure of 100 lbs. is so high that it could not be used in practice on account of the probability of obtaining a cloudy filtrate.

The break in the curves which occurs after approximately 2000 cc. of filtrate have come over represents the point at which the distance frames become completely filled with the precipitate. If more sludge be pumped in, it gets tightly packed around the inlets with the result that the entire filtering surface of the cloths is no longer effective and consequently the rate of flow decreases. As would be expected, this point occurs somewhat later with the higher pressure than with the low, since at high pressure the capacity of the frames is increased on account of the greater compression of the precipitate.

With the idea that the rate of flow might possibly be a power function of the pressure as well as of the volume of filtrate, we plotted the rate for a constant volume (1000 cc.) against the pressure, and taking the logarithms as before, obtained the straight line shown in figure 3. This indicates that such is actually the case, or to express the relationships mathematically,

$$R = K\frac{P}{V^n},$$

where R is the rate of flow in cubic centimeters per minute, V is the volume of filtrate in cubic centimeters, and K is a constant. For the series of runs above described, the calculated values of m, n and K will be found to be 0.270, 0.810 and 13,600, respectively, giving as the equation for the rate of flow at any volume of filtrate or pressure,

$$R = 13{,}600\,\frac{P^{0.27}}{V^{0.81}}.$$

From this equation, it is strikingly evident that instead of the rate of flow being directly proportional to the pressure as has hitherto been generally supposed,

[1] To economize space, only a small number of the recorded values have been given in this and in the following tables.

[1] As each of these runs was carried out at a constant pressure, $f(P)$ is, of course, a constant, and the equation becomes $R = K/Vn$. Taking the logarithm of each side gives us $\text{Log } R = K - n \text{ Log } V$.

it is for this particular sludge proportional to only approximately the fourth root of the pressure. Assuming, as is probable, that the rate of flow through a filter cake is analogous to that through fine capillary tubes where the rate is directly proportional to the pressure and to the square of the radius of the openings, this low coefficient is readily explained by the nature of the sludge here used. Owing to its non-crystalline character, it is very easily compressed, and consequently with the same amount of precipitate in the frames, at the higher pressure the passages through the cake would be expected to be considerably smaller than at the lower pressures. If this explanation is correct, then with a sludge containing a more granular precipitate the pressure coefficient should more nearly approach unity, and work to determine this point has already been started in this laboratory.

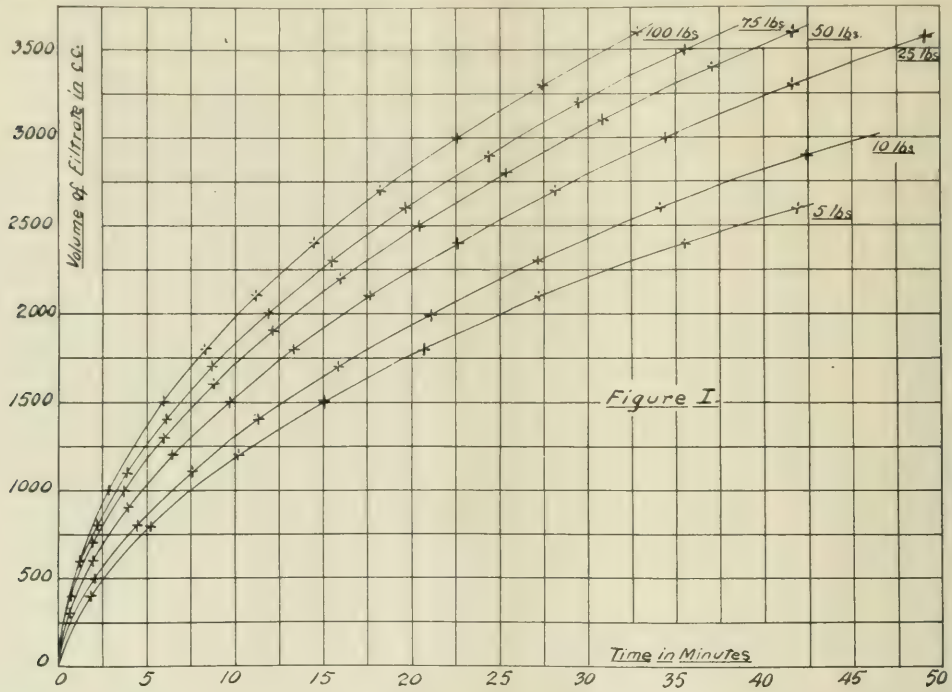


Figure I.

A study of these results makes it clear that all the problems in filter press design can readily be solved by their aid. The equation for the rate of flow having been established as

$$R = K\frac{P^m}{V^n},$$

it is only necessary to determine experimentally the values of K, m, and n, to be able to calculate the rate at any pressure or thickness of cake desired. From work that is at present being carried on in this laboratory, and from other data already on hand, it is known that these values vary very greatly with the nature of the precipitate, but for any particular sludge they are constant. To determine these values for industrial application, it is necessary to make only two trial runs at different pressures, and it is our opinion that these runs may be carried out inside of two hours on a small laboratory press such as was used in this investigation with results which may be depended on to closely approximate those of actual practice.

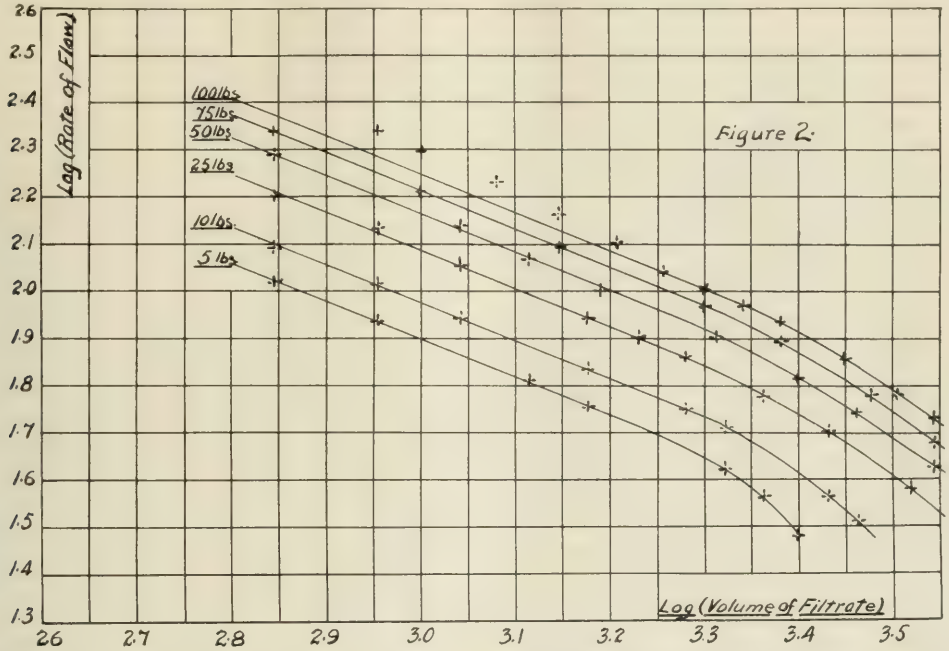
EFFECT OF VISCOSITY.

In commercial filtration, the viscosity is, as a rule, a pre-determined factor which cannot be varied at will. But it is very possible that the viscosity effect may be of considerable importance in determining the rate of washing, where the washing medium is usually less viscous than the original filtrate. Reasoning from the analogy already observed between flow through a filter cake and flow through capillary tubes, it would be expected that the rate would be inversely proportional to the viscosity.[1] To determine this point, and also to ascertain whether the viscosity has any effect on the pressure and volume coefficients, the two runs described below were undertaken.

These runs for determining the effect of viscosity were exactly the same, except that the amount of precipitate varied. An indefinite amount of sludge (about a liter and a half for the first run and a half liter for the second) was pumped into the frames at 25 lbs. pressure, and then filtrate alone was pumped through until the rate of flow became constant. By referring to Run No. 4, the volume of filtrate to which this rate corresponds can be readily ascertained. The filtrate was now diluted one-half with water and again pumped in until the rate was constant. Without changing the solution entering the press, the pressure was dropped to 5 lbs. and then raised

[1] The flow through a capillary tube is equal to $\pi r^4 P/8\mu l$, where r is the radius of the tube, l is the length, P the pressure, and μ the viscosity of the liquid. (Lamb, "Hydrodynamics," p. 544.)

again to 25 lbs., the rate being recorded for each pressure. The discrepancy which will be noticed existing between the rates at 25 lbs. before and after dropping the pressure is probably due to channels forming through the sludge when the pressure was relieved, and on this assumption the second rate has been accepted as the more comparable to the other values. Finally in the same manner, pure water was pumped in, and the rates of flow determined as before at 25 lbs. and 5 lbs. pressure.



From these runs, the following data were secured:

	Run A. Cc	Run B. Cc
Rate of flow with filtrate (at 25 lbs.)	87	167
Volume of filtrate corresponding to this rate as determined from Run No. 4	1515	675
Rate with diluted filtrate at 25 lbs:		
Before dropping pressure	92.3	174
After dropping pressure	100	175
Rate with diluted filtrate at 5 lbs.	20	35
Rate with pure water at 25 lbs.	109	180
Rate with pure water at 5 lbs.	21.5	36
Absolute viscosity of filtrate[1]	0.0124	
Absolute viscosity of diluted filtrate	0.0109	
Absolute viscosity of pure water	0.0096	

From these figures, the rate of flow is apparently approximately proportional to the viscosity as was expected, but owing to the fact that on account of the change in conditions experienced on dropping the pressure, the rate with straight filtrate is not strictly comparable to the other rates; too much faith should not be put in this conclusion in the absence of further confirmatory evidence.

It will be noticed that the rate of flow at 25 lbs. pressure is in every case just five times that at 5 lbs.; in other words, the pressure coefficient has become equal to one. This is directly in accordance with the explanation advanced for the low coefficient previously encountered, for in this case where the pressure is simply lowered and raised again without the addition of any more precipitate, it would not be expected that the size of the small openings through the cake would alter materially; consequently the rate of flow would follow the law for flow through capillary tubes where it is directly proportional to the pressure.

The values for the volume coefficient (n) as calculated from these runs are:

	n.
Straight filtrate	0.810
Diluted filtrate	0.692
Pure water	0.621

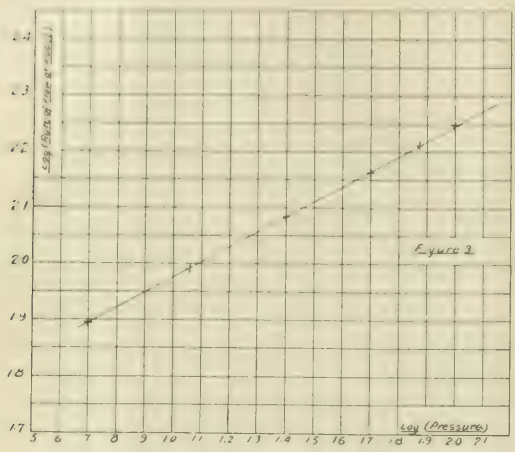
It must be understood that these figures are not to be considered anything but relative, since their absolute accuracy depends, of course, on the correctness of the value for the volume of filtrate which was taken from Run No. 4—a run made with a different batch of sludge. But though the above calculated figures for n are for this reason possibly considerably in error, nevertheless the relationship between them is correct, which is all that is essential. Comparing these values with the absolute viscosity of the solution, it appears that the volume coefficient is roughly proportional to the viscosity. This relationship is brought out by the following table:

	Viscosity.	n.	Viscos / n.
Straight filtrate	0.0124	0.810	0.0153
Diluted filtrate	0.0109	0.692	0.0158
Pure water	0.0096	0.621	0.0155

The reason for this unexpected relationship is very difficult to see, and it is unquestionably true that too much emphasis should not be laid upon results from preliminary experiments such as these. But it is hoped that by pointing out this apparent

[1] Viscosity determinations were made according to Gurney's method. (See *J. Am. Chem. Soc.*, **34**, 24.)

proportionality, other investigators will be led to try more exhaustive and accurate experiments which will afford an explanation for the phenomenon.



From the equation $R = K\frac{P}{V^n}$, it would be expected that K would vary inversely with the viscosity, but the effect of the above-mentioned variation in n is so great that the reverse is true. The calculated values of K are as follows:

Viscosity.	K.
0.0124	1310
0.0109	635
0.0096	410

These values of K are interesting chiefly as an indication of what may be expected to develop on further investigation of the subject.

The purpose of this article is twofold: First, to point out that, despite the popular theory, the rate of flow of a liquid through a filter cake is not as a rule directly proportional to the pressure and inversely proportional to the thickness of cake, but can be expressed by the equation $R = K\frac{P^m}{V^n}$, in which the constant and coefficients can be quickly and easily determined; and secondly, by outlining some preliminary experiments carried out in this laboratory to stimulate further investigation which will be able to explain the very interesting and unexpected relationships which apparently exist between the viscosity of the filtrate and the values of n and K.

RESEARCH LABORATORY OF APPLIED CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON.

IMPROVED SULPHURIC ACID CHAMBERS.[1]

By THOMAS H. NORTON.

While visiting the extensive works of the Union Fabrik Chemischer Produkte at Kratzwieck, near Stettin, I was afforded an opportunity to examine minutely two series of sulphuric-acid chambers recently constructed by the company. These are regarded as embodying the most advanced ideas of the day.

[1] Special report to Bureau of Manufacturers, Department of Commerce and Labor.

On October 10, 1910, three of the nine chamber plants were destroyed by fire. In planning for rebuilding, the director decided to adopt the essential features of the so-called Moritz system of chamber construction, as not only promising economy in future cost of production, but also offering exceptional facilities for rapid replacement of the missing units, even during the winter season. He was able to use the first series of chambers on March 15th and the second on April 4th of this year. The construction of the third unit did not begin until July.

The Moritz system was brought to the attention of technical chemists about four years ago. It was first introduced at Wasquetal, northern France, by the Société anon. des Etablissements Eyken et Leroy, with which the inventor, R. Moritz, is connected. The results obtained in a chamber system of 4,500 cubic meters were so satisfactory that several French and Belgian works utilized the new method when increasing their chamber capacity.

At present a large system of 8,000 cubic meters is under construction at Hainaut, Belgium, a smaller one of 4,000 meters at Elberfeld, Germany, and the third unit of the "Union" works (5,200 meters).

As a rule, in chambers constructed according to prevalent methods, the sides, the top, and the bottom of a lead chamber are supported by strong wooden beams. These timbers, while showing externally no change, are seriously affected by the radiation of heat from the adjacent lead walls. The temperature of the walls may attain 90° and even 100° C., and as a result the wood rapidly loses its strength, becomes brittle, and is warped. This leads to a dangerous strain upon the flaps along the walls. They are frequently torn off and the wall loses its shape. This tendency is heightened by the great difference between the coefficients of expansion of lead and wood. The thoroughly dry timber offers also an undesirable amount of very combustible material, as shown by the extensive fire at Kratzwieck in 1910 and the conflagration at the Wasquetal works in 1907.

Much more serious, however, is the increased corrosion of the lead chambers, due to the use of wooden supports. Those portions of the lead walls adjacent to the timber supports are prevented from radiating heat freely. This retards the oxidizing reaction in the immediate vicinity, while allowing the lead to be corroded more rapidly. Careful measurements of the thickness of the wall in different parts of a lead chamber, after the fires mentioned, showed that the portions of wall screened by a timber were on an average half a millimeter thinner than other sections of the chamber. This was in spite of the fact that the timbers were separated by spaces of 8–10 cm. from the lead walls.

An additional disadvantage results from the more rapid corrosion of the lead behind a beam, as leaks occur thereby most frequently at points where the repairs are difficult to execute. In some few works iron instead of wooden beams have been introduced. This obviates the distortion of the chamber walls, due to the warping of the wood, but does not diminish

the trouble arising from rapid corrosion and the difficulty in carrying out repairs.

With regard to the bottom of chambers, observation shows that corrosion is very pronounced along the lower edge, where the lead is bent upward. Here a zone of about 6 inches is peculiarly liable to rapid attack; and the same is true of the lower part of the side walls, which form the hydraulic joint. The direct cause of this quick corrosion is the thick flooring of wood necessary to support the weight of the acid, by retarding the radiation of heat from the surface of the lead.

The tops of chambers are ordinarily flat. The lead sheets are attached by flaps to overhead beams or hung upon iron rods or tubes. In both cases the same disadvantages exist as have been previously mentioned. A flat roof also favors the accumulation of dust, which in turn retards radiation. As a rule it is a matter of great difficulty to clean thoroughly the ordinary flat roof of an acid chamber.

The prevalent method of attaching the various sections of a lead chamber to its supports prevents almost entirely any uniform expansion of the different parts. In consequence of the heavy weight of the lead, and of the uneven expansion, there is a constant tendency toward strain about the flaps, and cracks that are exceedingly awkward to mend appear along the soldering lines.

All of these defects of the customary construction seem to be avoided in the Moritz chambers. The essential feature of such a chamber unit is a strongly built skeleton of structural iron, enclosing the chambers, which are suspended from overhead beams. The skeleton serves also as a support for the roof.

The main columns of this skeleton, which bear the weight of the roof, have been constructed in some cases of concrete or masonry. Preference is, however, given to iron, as involving less time in preparation and assuring greater strength. A tile roof is used. The outer walls of the structure are built of brick, laid between the upright columns. The bricks are placed edgewise, so that the walls are exceedingly light, 2.36 inches in thickness. No windows are required. An abundant use of panels of wire-net glass and of ordinary glass tiles in the roof affords all needed light. Some additional light and abundant ventilation are assured by numerous series of openings in the brick walls, the bricks being arranged in a lattice-like manner at distances of 3.937 inches from each other. Such an arrangement suffices to keep out snow and rain, while affording a maximum of air circulation for cooling purposes.

At Kratzwieck two units are located side by side, separated from each other by an aisle about 4 feet wide, and under a single roof. In other forms of construction there is a separate roof over each unit.

Great ingenuity is displayed in the manner of suspending the chambers from the skeleton framework. At intervals of 31.5 inches along the top edges (27.5 inches on the end sides) hooks of half-inch iron are attached firmly to the lead sheets. These hang by iron rods (1.57 by 0.24 inches) from the T girders overhead, and thus insure a complete, unhindered exposure of the side walls to the cooling action of the air. There is, however, a further addition necessary, in order to obviate any danger from expansion or contraction. Along the walls, likewise at distances of 31.5 inches (or 27.5 inches on the end walls), vertical flaps are soldered on tightly. Light iron rods, round or flat, pass through these, and are connected above with the pendant supports, while below they are attached, by means of spring hooks, to the upturned edge of the chamber floor. They give a ribbed appearance to the chamber walls and increase the cooling surface. While imparting a certain amount of rigidity, and preventing undue swelling outward, or inward depression, they still permit of free play for ordinary contraction, or the reverse, without any undue strain falling upon the soldered fastening of the ribs. The effectiveness of this rib construction is heightened by numerous horizontal connections, by means of iron rods, with the skeleton frameworks.

A similar principle is applied in the case of the top of a chamber. Here there is also a ribbed construction, and hooks at frequent intervals are connected by round iron bars with the girders overhead. All exposed iron parts are carefully protected from corrosion by a special paint.

In the shape of the chamber top we encounter one of the most striking innovations of the Moritz system. It is of a semicylindrical form to prevent the accumulation of dust, while avoiding "dead corners" inside the chamber, and their liability to frequent repairs, and assuring a more perfect circulation of air about its upper surface.

The lead floor of the chamber rests upon an under floor of iron plate 0.197 inch in thickness, and this in turn is supported by brick columns about 8 feet high. In some instances the constructors have used wood or ferro-concrete. In all cases, however, the upturned edge of the floor consists of iron plate, bent underneath to a distance of 9.8 inches. This is to insure the most rapid cooling at the weakest point in the construction of a chamber, where corrosion is most pronounced, and repairs involve a complete stoppage of manufacture. An identical method is used in supporting the lead mantles of the Glover and Gay-Lussac towers. Details are naturally much simpler, on account of the smaller size of the towers. Each tower shows eight vertical ribs.

There are certain theoretical considerations connected with the use of the rounded roof that deserve mention. In addition to the advantages attendant upon this particular shape, the inventor claims that it is a powerful factor in equalizing temperature, and consequently in insuring uniform chemical activity and production in all parts of a chamber. While there is little movement of air over a flat roof, there is, on the contrary, an active current over the surface of a curved roof, thus bringing about a more rapid cooling. In a chamber of rectangular construction the hotter gases accumulate at the top. With a curved roof the volume of such gases is reduced to a minimum. They are constantly drawn off by the

gyratory movement of the chamber's contents, due to external cooling, and descend steadily downward along the walls. An instance is cited from the observations made at Wasquetal upon the temperatures at three different points in the first chamber of a plant. Under similar conditions of external temperature, with the same pyrites, the same ovens, and the same towers, the temperatures observed at the three points in a rectangular chamber were 90°, 88°, and 86° C. In the chamber with curved top, which replaced the former, they were 75°, 75°, and 74° C. The more rapid cooling and the close approach to uniformity are noteworthy. The director of the works at Kratzwieck is, however, of the opinion that a more gently curved roof is quite as effective as one of semicircular shape and more desirable from several standpoints. In the plant now under construction he plans to modify this feature.

At the outset it must be noted that the cost of construction, per unit of cubic chamber space, is higher than by the old method. At Kratzwieck the additional cost was found to be about 33 per cent. This figure would vary according to local factors.

There seems to be no doubt of the manifest economy in space, frequently an important factor where chemical works are hampered in their development by lack of sufficient available area for building. At Kratzwieck the two units already built on the Moritz system occupy but two-thirds of the area formerly covered by three separate units before the fire. Yet these two units produce more sulphuric acid than the three units that were destroyed.

The next important economy is in the amount of nitric acid required to produce the maximum effect in the lead chambers. The newly erected plant of the "Union" yields daily about 7 kilograms of acid (50° Baumé) per cubic meter of chamber space. Formerly, at this rate of production, 0.7–0.8 kilogram of nitric acid (36° Baumé) was consumed for each 100 kilograms of chamber acid of the above strength. This consumption has now fallen to very nearly 0.5 kilogram. It is to be noted that 0.9 kilogram is a very common figure in German acid works. In 1900 the average consumption was 1.4 kilograms in American acid works burning pyrites. This loss of nitric acid is an important item in the cost of producing sulphuric acid. In Germany it constitutes 4–8 per cent. of the total cost. It is obvious that a saving of 1 or 2 per cent. in this direction constitutes a notable economy. The inventor guarantees a maximum loss of 0.6 kilogram where chambers are producing 7 kilograms daily per cubic meter. It may be mentioned in this connection that in the "Union" system water in the form of spray is admitted to the chambers in summer and in the form of steam during the winter.

Apart from the direct saving on the daily cost of production, the director of the "Union" works is confident from his study of the plant during the few months that it has been in operation that there will be ultimately a very material saving in the item of depreciation, through the prolonged life of the chambers, and the ease and simplicity with which any necessary eventual repairs can be executed.

A MODIFICATION OF THE FRARY ELECTRODYNAMIC STIRRING DEVICE.

By J. M. Knoll and W. R. Work.

Received March 14, 1912.

The use of a solenoid for the rapid determination of metals in the electrolytic way was proposed by Frary (*Journal of the American Chemical Society*, November, 1907, and in other publications). He employed the usual form of solenoid which is a coil of copper wire cylindrical in shape and hollow, and enclosed in an iron case. The beaker containing the electrolyte is put into the hollow space in the center of the coil and a current passed through the electrolyte in the usual way. At the same time a current through the solenoid produces a magnetic field in the region of the beaker which in conjunction with the electrolyzing current causes a rapid circulation in the electrolyte.

The disadvantages of this form of apparatus are that the electrolyte is not in sight and an inspection of the electrodes during the process of electrolysis is not easy. The solution becomes quite hot and in some common determinations this is not desirable. The use of a cooling coil complicates the apparatus.

MODIFICATION.

By actual measurements the magnetic field produced by a solenoid was shown to be practically as strong at the top of the coil as it is at any point in the interior, and an inch above the top it still amounts to 40 per cent. of this strength, gradually decreasing as the distance increases, as shown by Fig. 1. The lines

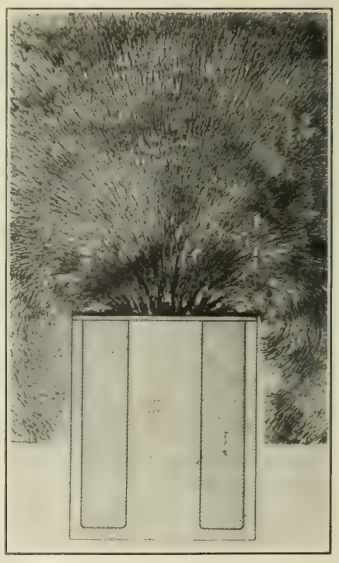


Fig. 1. Vertical Section through Solenoid and Diagram of Magnetic Field Above It.

of force which constitute the field pass without hindrance through glass, paper, wood, brass, etc., so it is a simple matter to put the coil of the solenoid around an iron core, cover the top with a suitable material and place the beaker containing the electrolyte on it. By using electrodes with bent stems a very simple

and convenient electrode holder can be used in conjunction with this form. Both electrodes are fastened to a small block which is raised with one hand while the wash bottle is used with the other.

The objection might be raised to our modification that on account of the strong field at the bottom of the beaker and the weak one at the top, most of the stirring would be at the bottom. It is true that the vigorous stirring does originate at the bottom, but on account of the free circulation, the upper part of the solution gets all the stirring necessary. In any event the solenoid stirring does not produce the commotion in the solution caused by a mechanical stirrer but nevertheless results can be obtained quickly. The average strength of the magnetic field measured in the region of the beaker is 700 gausses.

RESULTS.

(Frary has described in detail the speed and accuracy obtained by the use of a solenoid in electrolytic work.)

The four solenoids shown in Fig. 2 have been in use in the Chemical Department of the Pittsburg Testing

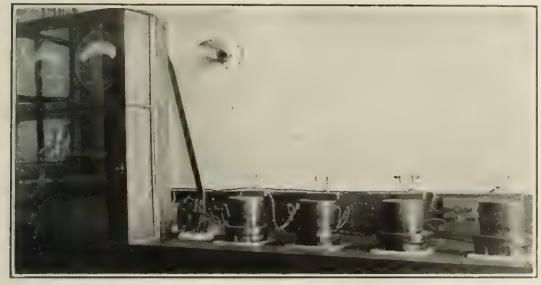


FIG. 2.—SOLENOIDS WITH MOVEABLE ELECTRODE HOLDERS IN POSITION

Laboratory for several months and are very satisfactory for the large variety of determinations we are called upon to make. We recognize the merits of the various forms of apparatus proposed for mechanical stirring but prefer our present equipment. We find it much more satisfactory than the stationary gauze electrode alone where a variety of determinations are to be made.

With stationary gauze electrodes in 125 cc. of solution containing about one gram of copper we allowed three amperes to pass for fifty minutes in order to be sure all the copper had been deposited. With the solenoid the same amount of copper is deposited in thirty minutes under the same conditions using the same electrodes. With a higher current the results can be obtained in less time.

PITTSBURGH TESTING LABORATORY,
CARNEGIE TECHNICAL SCHOOLS.

THE UNDERWRITERS' LABORATORIES EXTRACTION APPARATUS.

By HENRY J. CARY CURR.

Received April 16, 1912.

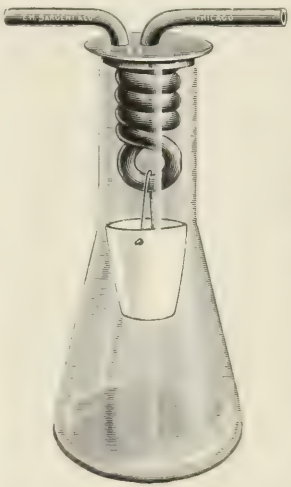
It has been found necessary in certain lines of extraction work to devise for routine work a method that is both rapid and convenient, such, for example, as the determination of certain extractable constituents of rubber insulation on wire, etc. In such a case the moisture content (generally less than one-half of 1 per cent.) is a negligible factor in the determination and may therefore be overlooked except in special cases where it is especially desired. Based on this ground the Chemical Department of the Underwriters' Laboratories at Chicago have spent several years in developing methods and apparatus to be used in a standard procedure for chemical tests of rubber compounds used on wires and cords.

Any form of extraction apparatus may be used, but it must conform to the following specifications: (1) "The extraction cup shall be surrounded by the vapor of the solvent at its boiling point." (2) "The condensed solvent shall fall directly on the sample." (3) "The outlet from the extraction cup shall be at the bottom only." (4) "No rubber or cork stoppers shall come in contact with the solvent." (5) "Sample shall be put directly into extraction cup without the use of a paper thimble—a disc of filter paper or its equivalent at the bottom of the cup being depended upon to hold back the solid part of the sample."

Following the manipulations of the above-mentioned methods it becomes necessary to extract into a tared flask which must be reweighed and which must therefore be of proportions and style suitable for admission to the bows and pans of an ordinary analytical balance.

Rapidity and efficiency of condensation together with ease of manipulation and installation as well as simplicity of construction and therefore low cost of maintenance and replacement were other points to be considered.

To meet these requirements a new apparatus has been devised and thoroughly tried out and is of exceptional merit.



It consists of a short, metallic, spiral-tube reflux condenser, whose inlet and outlet tubes project through a metal plate which serves the double purpose of a support for the condenser and a closure for the extraction flask. The flask is of rather conical form with a long neck and flat bottom. Two holes are bored on opposite sides of the upper rim of a porcelain Gooch crucible which is suspended from the condenser by passing through the holes a short piece of platinum or aluminum wire which also passes through the loop at the bottom of the condenser. The charge having been placed in the crucible, the condenser and crucible are placed in the neck of the flask, the water connections made and when a good flow of water has been

established, heat is applied to the flask and the action is carried on automatically.

The evaporated solvent is condensed on the spiral coil and drops into the crucible, passing through the sample into the flask where it is again volatilized and the cycle is repeated.

As the whole apparatus is only 6″ high and 3″ wide it takes up the minimum of space, and where much work of this character is done a battery of extractors and flasks can be arranged on a hot plate or water bath of very small dimensions, say two rows of ten or more flasks, in which case the bath can be furnished with a set of spring clips to steady the flasks when one of the set is removed. The water flowing from one condenser to the other only one inlet and one outlet is needed.

Copies of the Standard Methods alluded to above may be obtained from the Underwriters' Laboratories of Chicago; the apparatus from E. H. Sargent & Co., of Chicago.

CHICAGO

ADDRESSES

THE PRESENT STATUS OF THE GAS INDUSTRY AND ITS OUTLOOK.[1]

By Charles E. Munroe.

When speaking of the gas industry our mind naturally reverts to those public service corporations that are manufacturing gas for distribution and sale, and it is interesting to note that we are almost touching the centenary of their origin, an event which has proved of such importance in the development of civilization and in making life in dense communities feasible, and relatively secure, as to be worthy of commemoration; for, although, following Murdoch's demonstration at Redruth, in Cornwall, England, in 1792, several isolated plants for lighting houses and factories were built and operated, the gas industry as we now regard it, with its central producing plant connected by mains and services with a multitude of consumers began when, in April, 1812, a Royal Charter of Incorporation was granted to the Chartered Gaslight and Coke Company of London, England.

In the United States, although isolated plants of an experimental nature are recorded as having previously been erected at Newport, R. I., and Richmond, Va., this industry began with the chartering of a gas company in Baltimore, Maryland, in 1816.

GAS INDUSTRY.

Number of establishments	1,296
Capital	$915,537,000
Cost of materials used	52,428,000
Salaries and wages	33,316,000
Salaries	12,385,000
Wages	20,931,000
Miscellaneous expenses	27,757,000
Value of products	166,814,000
Value added by manufacture (products less cost of materials)	114,386,000
Employees:	
Number of salaried officials and clerks	13,515
Average number of wage earners employed during the year	37,215
Primary horsepower	128,350

PRODUCTS.

Total gas produced	[2]150,835,793,000	cu. ft.
Straight coal	[2]19,985,253,000	" "
Straight water	1,726,082,000	" "
Carbureted water	79,418,486,000	" "
Mixed coal and water	40,775,283,000	" "
Oil	8,688,860,000	" "
Acetylene	[2]25,186,000	" "
All other	216,643,000	" "
Coke	[2] 82,049,683,000	bu.
Tar	[2] 92,152,938,000	gal.

[1] Address before the Division of Industrial and Engineering Chemistry, Annual Meeting A. C. S., Washington, December, 1911.

[2] In addition, 27,558 thousand cubic feet of straight coal gas, 13,070 thousand cubic feet of acetylene gas, 44,347 bushels of coke, and 38,370 gallons of tar were produced for sale by establishments engaged primarily in the manufacture of other products.

The present status of this industry in the United States is approximately set forth in the preceding table, wherein the statistics given are those collected by the Bureau of the Census for the year ending December 31, 1909; they show to what enormous dimensions this industry has grown in this country in less than one hundred years.

In presenting these statistics I must, as I have on several previous occasions, call your attention to the limitations placed on census statistics, in common with all other bookkeeping statistics, growing out of the necessity for keeping each category carefully separated.

Thus while in the foot-note there is given the statistics for those establishments that manufacture "artificial gas for sale" as a subsidiary product, there is not included in the table or foot-note the natural gas produced for sale, since this is not manufactured, nor the blast furnace gas or producer gas, since while these are manufactured they are not produced for sale but are consumed by the establishments manufacturing them. Likewise, though the by-products coke oven gas produced for sale is included in the statistics of the table when such establishments are primarily engaged in producing gas for sale, yet the gas from the larger number of by-product plants, and also the coke and tar produced by them, is not included in the table since these products are chiefly consumed by the establishments of which they form a part. Such gas, however, as has been sold by these last mentioned establishments to gas companies appears in the table by value, though not by quantity.

A comprehensive treatment of all gas industries would include the statistics for gas from all these sources, and I hope to be able later to present them.

It is to be noted that the Chartered Gaslight and Coke Company and the Baltimore Gas Company made coal gas by the destructive distillation of bituminous coal. The table includes water gas, mixed coal and water gas, oil gas, and acetylene gas in addition to coal gas. In quantity, carbureted water gas exceeds them all, and if the straight water gas together with that used in compounding the mixed gas be also regarded, water gas greatly exceeds in quantity all other gases combined. There may be some little surprise at finding acetylene gas and oil gas carried in this account for they are not usually thought of as being handled by public service corporations, yet to-day there are a considerable number of smaller

communities having central acetylene plants, and as this condition carries these acetylene statistics into this account, other returns for acetylene, shipped in containers, are combined with them. Oil gas is more remotely connected with this category, for it is almost wholly, if not completely, sold in containers, but nevertheless it is more closely connected with this account than any other opened on the Census books, and hence is placed here. Besides, since the product is largely supplied to railway coaches, and thus enters as a factor in interstate commerce, the companies are quasi-public.

The history of the gas industry is a record of continued struggles. As Walton Clark has said: "The conception of a system of illumination comprehending a central source, and radiating lines of conduits; the measurement and recording of the service rendered as rendered, and the absolute and immediate control by the served of the time, period and measure of service, was as bold and startling as has occurred in the mind of man." The product was early known to possess poisonous properties and to form explosive mixtures with the atmosphere. Its manufacture was promptly observed to create nuisances. For fifty years its most potent competitors in the field of artificial illumination were tallow, wax, and sperm oil, and the producers, conveyors and merchandizers of these materials were active in proclaiming the evils and dangers attending gas lighting, and opposing its introduction and growth. Because of its advantages outbalancing its disadvantages and because of many inventions, through which these evils and dangers were reduced and its benign characteristics improved, it eventually overcame these competitors and outstripped them, only to be met by petroleum and petroleum refining which, through the many forms of lamps devised for the burning of its products, gave cheap and brilliant illumination.

Fortunately about this time, through the ingenuity of Tessie du Motay and of T. S. C. Lowe, the manufacture of water gas and especially carbureted water gas was made commercially practicable. Moreover, in 1856, Perkin had made his discovery of mauve. In 1867 Kekulé published his classic memoir which stimulated the utilization of coal tar. The Bunsen burner had become known and its value demonstrated. About this time the value of ammoniacal salts as fertilizers began to be recognized and in consequence, the tar and ammoniacal liquor began to assume commercial value, and, thus protected and fostered, the gas industry flourished and grew side by side with its competitor petroleum, and even fed upon the latter in that the cheaper petroleum distillates were successfully adapted to the carbureting of the water gas.

But in 1879 Edison gave to the world the first practical incandescent electric lamp and in a short time the commercial feasibility and advantage of this method of illumination became so markedly apparent that the gas industry was thought to be doomed. Yet a series of events regalvanized it and put fresh life into it. First in importance was the invention by Auer von Welsbach in 1886 of the incandescent gas mantle which he attached to the Bunsen burner and which had been so perfected by 1892 that the use of these mantles became so widespread that approximately 100,000,000 of them were manufactured in the year 1903, and a larger number annually since then. In 1881 the Siemen's regenerator was adapted to the Coppeé oven and the general type of by-product oven since styled Otto-Hoffmann was produced. In 1882 the Knab-Carvés oven was developed into the Semet-Solvay by-product oven, and through these and subsequent improvements in the designs and methods of operation of the by-product ovens and their accessories the cost of the manufacture of gas became greatly reduced. Moreover, by the adaption of the Bunsen principle by Fletcher, in 1883, and others, to burners of various kinds, gas heating became feasible, and the use of gas as a source of heat and power, as well as of light, promoted the growth and extension of the industry.

But the perfection of methods for low cost generation and distribution of the electric current and its utilization as a source of light, heat and power for almost every condition under which these forms of energy are employed for domestic, manufacturing and community purposes, has gone on in the last ten years with continued acceleration so that the gas industry to-day finds itself menaced at every point by this competitor, and in the power field finds the gas engine completely outranked in simplicity and certainty of operation, and cost of up-keep, by the electric motor. Wisely, most of the larger gas corporations have protected themselves by combining the generation and distribution of electricity with the manufacture and distribution of gas, thus removing a dangerous competitor from the field, while at the same time gaining an intimate acquaintance with each industry and keeping informed of the state of each art and the attitude of the community toward each product.

I sympathize with the owners of gas securities who anticipate a great shrinkage in the values of their holdings, but I cannot believe the chance of this occurring in the near future to be so likely as some may fear. It is true that to hold the field where active competition with electricity may arise or to prevent this competitor from entering the field, the price of gas must be reduced; but the profit can be maintained by reducing the cost of its production; this simply means, in most instances, the introduction of better, and in most cases, now known methods and devices, and in a more scientific management of the enterprise.

A first step may be taken in the employment of the chemical engineer to observe and check with his thermocouples, his burettes, and reagents, the operations of gas making and purification, and the character of the by-products and their derivatives at every stage of the operations. The expense involved in the employment of a wise and accomplished chemical engineer cannot fail to prove to be a profitable investment.

A second step may be taken in the reduction of heat losses whereby a saving may be effected in the fuel account, and the efficiency of the operators im-

proved too, for this is a feature in the manufacturing operations which, until recently, has been almost universally overlooked.

A third step may be taken in the more complete recovery of the by-products and their more complete utilization. This will lead to a more diversified industry and demand a larger measure of chemical knowledge and experience. It may be of interest to recall, what has already been recorded in our literature, that one gas establishment in the United States has, in addition to producing coke, tar and ammonium salts, entered on the manufacture of cyanides. But it tries the patience of the chemist to see the sulfur and other compounds going to waste in the purifying material when they can be usefully employed for so many different purposes.

A cheapening of cost throughout may be effected by the introduction of more modern plants. There is not time in which to go into details of the several systems but I may refer to the by-product coke ovens as having, through the size of their units the following advantages; the introduction of mechanical methods for handling coal and for charging and discharging the ovens; the ability to successfully make use of coals not before classified as gas coals; the better recovery and utilization of the by-products; and the cheaper production of gas. A difficulty in their use lies in the fact that they are primarily coke producers and that they can be employed profitably only where, as at blast furnaces, there is an assured market for this coke at a reasonable price. When, in 1906, I was engaged in the study of this industry I found its progress arrested by an inability to dispose profitably of the tar. It is worthy of note that in the interval that has elapsed, the proof of the value of coal tar as a binder for road material has been so well demonstrated, and the "good roads movement" has met with such acceptance, that an active market has been made for coal tar and the building of by-product coke ovens has proceeded while the outlook for the disposal of tar from gas works has improved. Beginning with the by-product plant at Everett, Massachusetts, gas from such plants has been distributed for sale when they were conveniently adjacent to large consuming communities, and to a market for the coke, but a combination of these prerequisite conditions is not common.

Fortunately there have now been devised, both by Koppers and by the Semet-Solvay Company, gas ovens which combine with the proved advantages of the by-product oven a method of utilizing such a portion of the coke in further manufacture that most neighborhood markets can absorb the residue at a good price. So far as I am aware the Semet-Solvay oven is yet undemonstrated but the Koppers gas oven has been built and operated and it has been ready to contract to put gas made in this oven into the holder at a cost of but 6.3 cents per thousand cubic feet. At such a cost gas can for a long time yet compete with electricity.

The development of flameless incandescent surface combustion may fortify the gas industry. The applications of gas by this means to domestic uses, manufacturing and metallurgical purposes and to the generation of steam, are most impressive. This discovery and invention is now being subjected to severe scrutiny and test and if it proves to be what it now appears to be, it is expected to be of more benefit to the gas industry than Welsbach's invention of the incandescent gas mantle.

Moreover, the recovery of the sulfur whose loss in the past has been mentioned and deplored seems now commercially possible since means for its utilization, which have been demonstrated as feasible and operative in the laboratory are now being tested on a commercial scale in the factories, Burkheiser's recovery process being operated in connection with the Flemalle Grande coke ovens near Liege, Belgium, while Walther Feld's rival process is being employed at the gas works in Königsberg, Germany. Both aim to produce ammonium sulfate from the ammonium compounds in the gas liquor and the sulfur compounds obtained from the coal. Feld's process is of special interest to the theoretical chemist in that the formation of the commercial product sought and the saving of the useful matter accomplished is effected through the aid of the tetrathionates and the controlling under manufacturing conditions of the reactions through which they are formed and those into which they will enter.

An unexpected competitor to the gas industry in its commercially successful utilization of its by-products is the alcohol industry which produces as a by-product enormous quantities of slops, the major portion of which have gone to waste, for it is found that through the action of the enzyme, amidase, upon the diamido acids present in these distillery residues, ammonia and propionic acid are formed. Being an enzymatic reaction no expensive or complicated plant and no difficult or dangerous manipulation is required in the process. This process, known as the Effront process, produced at the Nesle distillery, from the molasses vinasse, resulting from the production of 100 liters of alcohol, 35 kilos of ammonium sulfate and 35 kilos of the fatty acid; and from the beet-root vinasse representing 100 liters of alcohol it produced 16 kilos of ammonium sulfate and 12–14 kilos of fatty acid. In the process, the diamido nitrogen was completely converted into ammonia, no amines or ammonia compounds resulting.

The competition from this quarter is prospective but it is not likely to materialize immediately. For the consolation of the afflicted manager of gas works it may be said that the microörganisms and their enzymes may be commercially employed in the resolution of some of his troubles. Very properly the denser and more progressive communities are forbidding him to discharge his polluted effluents into the adjacent water courses. I imagine nothing can be more enraging than to be thus enmeshed, but these microscopic bodies may be put under his command to not only so purify these effluents that they become quite innocuous, but to also give such a commercially valuable return in the product as to almost if not quite repay the cost of the operation.

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CURRENT INDUSTRIAL NEWS

SELENIUM GLASS.

Selenium, to the extent of about 11,000 lbs. annually, is produced by three American firms from the anode muds in electrolytic copper refining. The demand, which is not large, is practically limited to manufacturers of red glass and red enameled ware; but while the use of selenium as a means of coloring glass was patented twenty-one years ago by F. Welz (*Ber.*, **25**, 819), very little has been published on selenium glass. It is for this reason that the paper by Fritz Kraze in *Sprechsaal*, **45**, No. 14, 214–6; No. 15, 227–8 (1912) is of great interest to the glass manufacturer; accordingly, it is abstracted at some length.

Welz used selenium or a compound of selenium and cadmium sulphide for the production of rose, red and orange colored glasses (see, in this connection, *Eng. Min. J.*, December 18, 1897, 731); but an enquiry in the "Fragekasten" of the *Sprechsaal* showed Kraze that these mixtures were not yet satisfactory. He gives as a good composition for coral-red corresponding to Kaiser-red glass (see *Sprechsaal*, 1911, 707): 100 kg. sand, 20 kg. soda, 8 kg. potash, 7 kg. lime, 0.5 kg. borax, 13 kg. cryolite, 300 grams selenium, 700 grams cadmium sulphide, and 230 grams sulphur. Similarly, for a transparent yellow-red glass, 200–300 grams selenium and 60 grams uranium oxide with 100 kg. sand, 12 kg. soda, 16 kg. potash, 20 kg. minium, and 10 kg. limestone, are recommended. The use of selenium and uranium oxide in the manufacture of orange-yellow glass, was patented in 1893. Uranium-selenium glass shows a green color in reflected light, while it is yellow-red in transmitted light (cf. uranium glass).

Spitzer patented a process for the red coloration of glass by the use of selenites and selenates (*Ber.*, **27**, 777). These compounds are more suitable than metallic selenium, since they are more stable in the heat of the furnace, and are in consequence less likely to become lost through volatilization and oxidation. New shades of color are obtained by the use of selenium and selenium compounds with gold (*Ibid.*, **28**, 195), or with silver, opacifying metallic oxides and certain minerals, such as cryolite, fluorspar, various phosphates, etc.

Even if elementary selenium is incorporated into the glass batch, it dissolves in the clear fusion without producing any coloration; doubtless it is oxidized and exists in the form of dioxide in a colloidal state. A reducing agent is necessary if a red selenium glass is to be obtained. Arsenic trioxide will effect the reduction of selenium compounds dissolved in glass, and the same reaction occurs with corresponding amounts of powdered charcoal or in fusion in a reducing atmosphere. With glasses fused with sodium selenate, Kraze always obtained a red coloration following an addition of arsenic trioxide corresponding to the reduction to selenium.

"All formulas including saltpeter for red selenium glass are absurd;" in fact, the use of saltpeter "does not seem to apply even in lead glass colored with selenium" (*Sprechsaal*, 1911, 142), for there will always be an oxidation of the selenium present, giving rise to ineffective selenium (colorless dioxide) and occasioning considerable loss. Kraze failed to obtain a color with a batch of the following composition: 100 kg. sand, 15 kg. potash, 15 kg. soda, 12 kg. marble, 6 kg. minium, 3 kg. saltpeter, and 125 kg. selenium.

Kraze concluded that if the red color of selenium glass is due to the separation of red elementary selenium, then there must result an evolution of hydrogen upon treating the glass with concentrated hydrofluoric acid. Investigation showed a simultaneous formation of hydrogen selenide, which could only be attributed to the presence of a selenide in the glass examined, No. 1 of the experiments given below.

Glasses decolorized by means of selenium possess an unusual clearness and brilliancy. The use of selenium as a decolorizing agent (sodium selenate is generally used) is claimed in German Patents 63,558, 78,565, and 88,615. Careful experiments have shown (see Miskowsky, *Keram. Rundschau*, **18**, 457) that the ratio of ferrous oxide to decolorizing agent is 1 : 0.000208 for selenium, which acts as a decolorizer by producing a complementary color which "covers" the green tint imparted to glass by iron oxides. (Selenium-manganese is now being marketed in the United States as a glass decolorizer.) Kraze found that the undesirable red tint, due to too much selenium in decolorized glasses, was removed when arsenic was added to the molten glass, which showed that arsenic acted as a reducing agent.

In the experiments made by Kraze, the following types of glass were placed in a Seger oven in chamotte crucibles and mixed with sodium selenate or selenium:

No.	I.	1.7	K_2O	CaO	9.8	SiO_2				
No.	II.	1.7	Na_2O	CaO	9.8	SiO_2				
No.	III.	1.18	Na_2O	CaO	6.94	SiO_2				
No.	IV.	1.53	K_2O	CaO	5.4	SiO_2				
No.	V.	1.53	K_2O	BaO	5.4	SiO_2				
No.	VI.	1.53	Na_2O	BaO	5.4	SiO_2				
No.	VII.	1.53	K_2O	ZnO	5.4	SiO_2				
No.	VIII.	1.53	Na_2O	ZnO	5.4	SiO_2				
No.	IX.	1.49	K_2O	CaO	9.8	SiO_2				
No.	X.	1.49	K_2O	BaO	9.8	SiO_2				
No.	XI.	1.49	K_2O	ZnO	9.8	SiO_2				
No.	XII.	1.49	K_2O	PbO	9.8	SiO_2				
No.	XIII.	1.49	K_2O	CaO	9.3	SiO_2	.	0.5	B_2O_3	
No.	XIV.	1.49	K_2O	CaO	9.47	SiO_2	.	0.33	P_2O_5	
No.	XV.	1.49	K_2O	CaO	9.3	SiO_2	.	0.5	SnO_2	
No.	XVI.	1.49	K_2O	CaF_2	0.3	Al_2O_3	.	9.8	SiO_2	

According to the calculation of the mixtures of types I–XVI, all contained 100 parts by weight of quartz, in order to measure the proportion of added selenium recommended by Schuster & Wilhelmy A.-G. for the production of rose-colored glass. According to this firm, 300–350 grams sodium selenate or 100–120 grams elementary selenium are used with 100 kg. sand.

No. I.—The crude mixture contained by weight: 100 quartz, 40 potash, 17 limestone. Of this mixture 157 grams were fused with 0.3 gram sodium selenate. On the first run, 3 hours after heating the Seger oven, the glass was still colorless. It was then treated with 0.5 gram arsenic, and after 30 minutes another test was made. The result was a completely fused glass with a very faint red color. This molten glass was next well-stirred and 1 hour after the previous test was found to be colored red. After another hour the color remained unchanged. It was next mixed with 0.6 gram more arsenic, which produced a deep red color; and, in 15 minutes, with the addition of another gram of arsenic, the color remained unchanged. This experiment showed that the red colored selenium separated out under strong reducing influences, the color increasing until the completion of reduction.

No. II.—An equal molecular weight of soda was substituted for potash; and the mixture contained 100 grams quartz, 31 grams calcined soda, and 17 grams lime. This time 0.5 gram selenium was added. After 2 hours, the glass was colorless; the addition of arsenic an hour later gave no result, and the glass finally became greenish without any noticeable red tint. These experiments showed that the soda-lime glass was unsuited for selenium coloring; the formation of a colored sodium selenide had not taken place. The green color observed was traced to dissolved ferrous silicate, resulting from the iron rod employed in stirring.

No. III.—This corresponded to a glass composition according to Tscheuschner and was selected in order to try a high-alkali glass: 100 grams quartz, 30 grams calcined soda, and 24 grams calcium carbonate were fused with 0.3 gram sodium selenate. After 3 hours, the glass was incompletely fused, very opaque,

but clouds: rose-colored, being even stronger than No. I before the addition of arsenic. The glass became slightly transparent 30 minutes later, but the red color had disappeared, after another half hour there still remained some unfused matter, but otherwise the glass was clear, although it possessed a greenish tint. An addition of 0.5 gram arsenic was now made, and the result was a clouded and intensely green colored glass; the green color persisted until clear fusion. Another addition of 0.5 gram arsenic gave a pale but still green glass. These fusions showed, as in the case of No. II, that soda-lime glass was hardly suited for selenium coloring, even though the greater lime content as compared to the soda present, was somewhat favorable for coloring at first. The increase in depth of the green color after the addition of arsenic was ascribed to a reduction of ferric silicate.

No. IV.—100 grams quartz, 65 grams potash, and 31 grams calcium carbonate were fused with 0.5 gram selenium. The iron oxide (from the rod) altered the red color of the selenium. An addition of 0.5 gram arsenic brightened the glass, and further additions served to produce ferrous oxide, the green color of which, with the red color of the selenium, produced the decolorization. The cold glass was bright yellow-brown, although it had a rose tint.

No. V.—The batch contained 100 grams quartz, 65 grams potash, and 60 grams barium carbonate, making a glass which fused easily: 0.5 gram selenium was added, and before fusion an addition of 1.5 grams arsenic was made. After 2 hours, the glass was bright and possessed a coffee-brown color and a rose shade. After 30 minutes, 1 gram arsenic was added, whereupon the glass rapidly became colorless, with only a weak brown tint. Further additions of arsenic produced a green color. The arsenic had finally caused a complete reduction of ferric oxide to ferrous oxide and consequently a green color; the selenium had been volatilized, although probably barium selenide was formed to a certain extent.

No. VI.—The batch contained 100 grams quartz, 50 grams calcined soda, 60 grams barium carbonate, and 0.5 gram selenium. The addition of arsenic was made as in No. V. The first result was an orange-brown, crystalline glass; after another addition of arsenic (1 gram), it became colorless. The complementary effects of the colors entered in here, for on repeated additions of 1 gram arsenic, the glass became very green colored.

No. VII.—The fusion was made with 100 grams quartz, 65 grams potash, 25 grams zinc oxide, and 0.5 gram selenium. After $2^1/_2$ hours, the glass was clear and of a deep brownish yellow color. The addition of arsenic failed to produce a change in color after 15 minutes; a second addition gave rise to a yellowish gray tint; and a third addition caused no change but a slight brightening. Kraze was led to believe that zinc selenide was formed in this experiment.

No. VIII.—100 grams quartz, 50 grams calcined soda, 25 grams zinc oxide, and 0.5 gram selenium. The results obtained were similar to those in No. VII, except that the clarification occurred after 3 hours and the color changes were different. After the first addition of arsenic, the color change was to yellow, and further additions effected no change in color and only a slight clarification. A red tint was never noticed.

The following tests were decidedly more acid than the preceding and the glasses were similar to potassium glasses of the type:

$$1.49\ K_2O.RO.9.8\ \text{acid.}$$

In the previous tests the acids entered into the composition solely as silica; in the following difficultly fusible, acid glasses were experimented with for comparison.

No. IX.—This was a composition for Bohemian crystal glass taken from Hohlbaum's *"Zeitgemässe Herstellung, Bearbeitung und Verzierung des feineren Hohlglases."* The batch of 100 grams quartz, 35 grams potash, and 17 grams calcium carbonate was fused with only 0.1 gram selenium. Three hours after heating the furnace, test 1 showed no unfused parts and was deep brown. 2 hours after, tests 2 and 3 possessed the same color. The addition of 0.5 gram arsenic, however, caused a change to a pretty red (test 4). The rose color did not change after $^3/_4$ hour (test 5), and even remained after repeated additions (2.5 grams) of arsenic (test 6). Even after 30 minutes later, following an addition of arsenic (0.5 gram), no change in color was observed. The results of this experiment showed that the desired color had been obtained with very small amounts of selenium (0.1 gram). Hence the results agreed with those of No. I, for the measured addition of sodium selenate (40 per cent. salt) used in the latter corresponded to 0.12 gram selenium; but glass No. I, with less silica, did not assume a rose color so rapidly as No. IX. Therefore, it seems that the acid content of the glass plays an important part in developing the red color. Nevertheless, it must not be considered that sodium selenate requires more energetic reduction for red coloring than selenium.

Kraze also fused the batch of No. IX with 0.2 gram of selenium, with 1 gram selenium, and again with double and five times the amount. What he expected did not occur: he red coloration did not become intensified from an increase in the selenium content, and the rose color resulting from an addition of 0.1 gram selenium could not be distinguished from that from 0.2 gram selenium—in fact, both glasses were colored even more strongly than when 0.5 gram selenium was used.

No. X.—In this experiment lime was substituted by barium oxide, but otherwise the glass was the same. The batch was: 100 grams quartz, 35 grams potash, 33 grams barium carbonate, and 0.2 gram selenium. The first test had hardly been fused before it showed a rose tint. Two hours after the gas oven was started, the glass was thoroughly fused, but the rose color was brown tinted. Four hours later, tests showed that the product was somewhat brighter.

No. XI.—A more acid zinc glass than No. VII was obtained by substituting zinc oxide for barium oxide. The batch consisted of 100 grams quartz, 35 grams potash, 14 grams zinc oxide, and 0.2 gram selenium. Tests showed that at the beginning of the fusion there was a very weak rose tint, but the melt later became absolutely colorless; the addition of arsenic did not cause the least coloration.

No. XII.—Composition: 100 grams quartz, 35 grams potash, 39 grams minium, and 0.2 gram selenium. After 4 hours fusion, the tests showed a yellow glass, but later brownish yellow, and finally a glass colored a little more intensely.

The next three experiments were again with potassium—lime glasses, but boric acid, phosphoric acid, or stannic oxide was in part substituted. Replacement of part of the silicic by boric acid in the acid potash glasses diminished the red color; and phosphoric acid and stannic oxide acted in a similar manner and to a greater extent. Replacement of the lime by fluorspar gave only a colorless glass, owing, no doubt, to the volatilization of the selenium as fluoride during the fusion.

Kraze promises to investigate the existence of selenides in colored selenium glasses.

HEAVY OIL ENGINES.

The following is an abstract of an address by Capt. H. R. Sankey before the Royal Society of Arts, April 29, 1912:—

Some twenty years ago there was only one form of oil engine, of which the Hornsby-Akroyd and Priestman could be taken as types. These engines required external heat at starting for the evaporation of their fuel and worked on paraffin. In 1890, Daimler invented the petrol-engine, which worked with petrol of a specific gravity of about 0.68 and which required no external heat for the evaporation of its fuel. Seven years later Diesel introduced his engine, which worked with heavy oil and required no external heat, as the fuel was mechanically "pulverized" instead of being evaporated.

At the present time, two classes of oil-engines are in use, *viz.*: light-oil engines, which use fuel capable of forming explosive mixtures at ordinary temperatures and possessing a density of 0.68–0.72; and heavy-oil engines, which use fuel requiring high temperatures or mechanical "pulverization" for the formation of explosive mixtures, and possessing a specific gravity of 0.8–0.9. Of the heavy-oil class, the Diesel engine, which has received much space lately in the technical press, is the most important type. In it the compression occurs entirely on a charge of air, into which the fuel is afterwards injected, so that there is no danger of pre-ignition, and compression pressures up to 450–500 lbs. per sq. in. can be used. It is, in fact, in its high compression that the great efficiency of the Diesel engine lays. In the semi-Diesel type of engine, in which, after compression of air, the fuel is injected into a hot bulb, there is no danger of pre-ignition, but compressions up to about 200 lbs. per sq. in. are usually found to be sufficient to ensure ignition.

In the Diesel engine admission occurs at constant pressure and exhaust at constant volume, as compared with the gas-engine and petrol-engine, in which admission takes place at constant volume. This difference gives the Diesel engine an advantage, since there is a greater difference between the upper portions of the actual and theoretical diagrams in the two cases. The economy of the Diesel engine is also largely accounted for by the high compressions, up to from 450–500 lbs. per sq. in., which can be used. The temperature reached in the cylinder of a Diesel engine is usually about 1200° F. With a 2-stroke cycle gas-engine there is danger that some of the new working charge may be blown out of the exhaust by the scavenging air, but in a Diesel engine this can not happen, so that the Diesel may be regarded as essentially a 2-stroke engine.

According to *Industrial Engineering*, **11**, 401, the thermal or indicated efficiency of the Diesel engine of to-day reaches 48 per cent., while the effective or brake efficiency reaches, in some cases, 35 per cent. of the heat value of the fuel. This engine converts the heat of the natural fuel into work in the cylinder itself, without any previous transforming process.

Allner (*J. Gasbel.*, **54**, 321) reported that tests on a 100 h. p. Diesel motor showed vertical-oven tar was a very satisfactory fuel for this type of engine; later (*Progressive Age*, **29**, 481) it was pointed out that tar fuel was the least expensive for Diesel engines and that with slight changes in the engine, no difficulty was experienced in using it; and Allner has more recently pointed out (*J. Gasbel.*, **54**, 1025) that the present practice in using tar is to assist ignition by spurting into the cylinder about 5 per cent. of gas oil just ahead of the tar. Recently, however, it has been found possible to operate on tar oil and avoid the use of even this small amount of gas oil, and quite lately it has been ascertained that a 40 h. p. Diesel engine may be operated by the use of raw tar itself, using both vertical oven tar and certain kinds of retort oven tar, and wholly avoiding any use of ignition oil.

THE CLASSIFICATION OF SOAPS.

With the object of classifying different soaps on a commercial scale, the Commission appointed by the Italian Union of Soap Makers has proposed to divide them in the order of their requirements. Gianoli reports as follows concerning the recommendations of the Commission [*Chem. Trade J.*, **50**, 465 (1912)]:

1. PURE SOAPS OF THE FINEST QUALITY.

(*a*) *Boiled Soaps.*—Hard, soft, floating, white and dyed, scented or unscented; not liable to change color or to become rancid; completely soluble in water and in alcohol; and constituted by a combination of soda and fatty acids when this is insoluble in sodium chloride solutions at 15° Bé., *i. e.*, free from oxy-fatty acids, and in which the total percentage of hydrated fatty acids, non-siccative, is not less than 60 per cent. Free from unsaponified glycerides, hydrocarbons, wax, alkaline and metallic soaps; not more than 0.3 per cent. free sodium hydroxide; not more than 1.5 per cent. total mineral matter; not more than 2 per cent. foreign organic matter (coloring matter, perfume, or fatty acids of low molecular weight).

(*b*) *Resin Soaps.*—Boiled with not more than 15 per cent. of colophony, and otherwise corresponding to the requirements assigned to the preceding.

(*c*) *Mottled and Marbled Soaps*, in which the proportion of hydrated fatty acids is not less than 55 per cent., and the total free alkalies, carbonates, sulphates, and alkaline silicates do not exceed 3.5 per cent.

2. CURRENT SOAPS OF INFERIOR QUALITY.

Hard or soft, plain or marbled, containing, or not containing, alkaline mineral detergents, organic or mineral fillings in quantities greater than 3.5 per cent. when the soaps contain 33 per cent. humidity—namely, soaps containing carbonates and alkaline silicates, talc, kaolin, asbestine, fossil flour, or sugar, starch, fecula, hydrocarbons, etc. Soaps manufactured cold or hot with fatty acid or glycerides of any nature, with or without resin.

3. DRY SOAPS.

Soaps which do not give more than 20 per cent. of water when exposed for 3 hours to a temperature of 105–110° C. after being pulverized with 10 times their weight of powdered glass.

The soap classifications hitherto published have been generally based on the methods of manufacture. The above classification seemed to the Italian Commission to more nearly meet the requirements of the analyst and consumer. What the latter desires to know is the peculiar character of the soap he is buying, and not how it is made. Consequently, to satisfy the trade, the limits within which the composition may vary must be specified.

THE SPONTANEOUS COMBUSTION OF CHARCOAL.

In 1911, there were 64 reported fires in the transportation of charcoal in the United States, and of these 63 were evidently caused by spontaneous combustion. During 1911, experiments on the spontaneous heating and ignition of hardwood charcoal were started at Straight, Pa., and at Westline, Pa., by the Bureau for the Safe Transportation of Explosives and other Dangerous Articles. The charcoal, after varying treatment as to cooling and air exposure, was loaded into box cars, and the temperature of the interior of these cars was observed at intervals to detect any increase in temperature. From the incomplete series of experiments performed, it was reported (Bureau of Explosives, *Report* No. 5, February, 1912, p. 47) that "no conclusions can be drawn as to the relative efficiency of various periods of cooling and airing. In no case was there any ignition or an increase of temperature approaching ignition. In every case but one there was a noticeable rise of temperature, which can be ascribed only to the action of air on the cold charcoal, and not to any residual sparks or fire." The figures obtained so far have not shown that wetting the charcoal increases the heating effects, although it is the general belief that heating more frequently occurs in damp weather. "To attain absolute security from fires of spontaneous origin it is necessary to store the charcoal in the open till such time as it attains its equilibrium with regard to absorption of air"—an impracticable procedure, so "the logical alternative is to supplement the best present practice of cooling, airing and storing in open cars for 24 hours prior to shipment by a safe method of ventilation of cars during shipment."

The experiments on the spontaneous combustion of charcoal recently published by the National Physical Laboratory (*Report* for **1910**, 85; **1911**, 86) were conducted in an electrically heated oven, in which 1 cu. ft. of the charcoal was exposed to a uniform temperature (constant within 1° C.), measured by

means of thermocouples. The charcoal was surrounded by an air space about 3 inches wide, and the oven could be closed air tight or a current of air of any desired velocity passed through it. Experiments with flake charcoal showed that with air currents ranging from 5–62 cu. ft. per minute for 1 cu. ft. of charcoal, spontaneous combustion occurred at temperatures of from 90–110° C., while at lower temperatures no signs of spontaneous heating could be observed. Additional experiments showed that in a current of air containing 5 per cent. sulphur dioxide, spontaneous combustion of the charcoal took place after some hours; therefore, there is risk of danger in using sulphur dioxide for disinfecting rooms, etc., where charcoal is present in the walls. It is reported that decayed wood appears to be much less inflammable than charcoal.

ARTIFICIAL RUBBER FROM SEAWEED.

A product, now being marketed under the name "Seagumite," said to be non-inflammable, damp-proof, and unaffected by heat or cold, and to be expected to provide a substitute for rubber and leather, is the subject of a patent recently issued to J. S. Campbell, of London (English Patent 5395, 1911). His invention relates to improvements in the production of a substance having the characteristics of rubber and capable of vulcanization. It had previously been proposed to treat marine plants, lixiviated by acidulated water, with alkalies such as ammonia; and it is said that the material thus produced has, after impregnation with siccative oil or dissolved india-rubber, been found suitable for use in the whalebone industry. The Campbell process consists in boiling washed and crushed seaweed in steam-jacketed pans with ammonia for about 45 hours, 1 gallon of ammonia (specific gravity, 0.88) being used for 5 cwts. of seaweed; drying in an agitating apparatus, to which heat is applied, and during agitation adding 1 gallon of a mineral or vegetable oil, as rosin oil; adding next a vulcanizing substance, such as sulphur, and subsequently mixing the whole mass with 25 per cent. by weight of a glutinous or resilient binder, as pontianac gum, jelutong, gutta-percha, or reclaimed rubber waste. The whole is then heated for 1 hour and finally dried in a vacuum pan or press. Prior to removing and drying, a preservative, as wood or bark extract, may be added to the amount of 0.85 per cent. by weight of the seaweed used.

The Campbell process seems to be primarily dependent upon the formation of ammonium alginate. Algin in its soluble forms is recognized as having probable value as an agglutinant, and a substance resembling gutta-percha may be prepared from the alkaline alginates and shellac.

"TEMPERED COPPER" TOOLS.

According to *The Engineering and Mining Journal*, **93**, No. 20, 986, the copper-cutting instruments of the Tarascans, found in the Balsas River ruins in Guerrero, are so hard that they would turn the edge of a modern knife, and it has been claimed that these people, along with the Aztecs and Toltecs, possessed the secret of tempering copper. On the other hand, copper knives and axes, found at Atcopotzalco, are so soft that they can be cut with an ordinary pocket knife. Analysis showed that in all three localities the copper implements were of the same composition as the copper ores found therein. The blades from Guerrero, which are hard and apparently tempered, were made from the natural ore carrying nickel and cobalt, thus rendering the smelted alloy steel-like in hardness. Thus, the natural product gave an alloy of great hardness when heated and sharpened, while the other ores of practically pure copper, when smelted, resulted in implements which were soft and inferior in cutting value. The sharp cutting implements were therefore the result of Nature's handiwork, and it is indeed very questionable whether these people possessed the secret of tempering.

THE PURIFICATION OF AIR BY OZONE.

Nature, **89**, 304, states that the system of ozone production and distributing plant installed for air purification and ventilation on the Central London Railway is a plenum one, and consists of Sirocco fans placed at each of the underground stations, except that at Shepherd's Bush. The total air supplied to the tubes is about 80,000,000 cu. ft. per day. Each fan draws its air through a filter screen, and works in conjunction with an ozone-generating plant. The latter consists of mica sheets with metallic gauze on each side, stacked side by side, and energized by alternating current at about 5,000 volts, in such connection that a silent discharge passes between the various plates, so that air passing between them is ozonized. The ozone generator is supplied with a small transformer, which in turn is supplied with 380 volts alternating current from a small rotary converter. The converter is connected on its direct-current side to the 550-volt lighting circuit of the railway.

THE USE OF COKE-OVEN GAS.

Cooper (*J. Gas Ltg.*, **118**, 107) states that in Germany the towns of Waldenburg, Altwasser, Salzbrunn, Essen, Dortmund, and Mülheim have been supplied for some time with gas from the neighboring coke-oven plants. The entire supply of gas for Mülheim-on-the-Ruhr and for Barmen is obtained from two coke-oven plants. The installation consists of 50 Koppers' horizontal regenerator ovens, each of which is capable of taking a charge of 8–10 tons of coal; the period of carbonization is 24 hours and only the richer portion of the gas (that evolved from the second to the twelfth hour, representing 50 per cent. of the yield) is used for distribution. During this time one oven will produce 70,600 cu. ft. of gas possessing a calorific value well over 600 B. t. u. per cu. ft. and costing $0.17 per 1,000 cu. ft. The gas is purified from hydrogen sulphide by the town authorities and distributed.

THE PRESERVATION OF WOOD WITH "BELLIT."

In order to increase the preservative effect of sodium fluoride on wood, it is now being mixed with nitro-phenols. According to Nowotny (*Oesterr. Chem. Ztg.*, **15**, 100; cf. *Idem*, **13**, 81), one of these mixtures, "Bellit," consists of 90 parts of 90–95 per cent. sodium fluoride and 10 parts of dinitrophenol-aniline. The latter compound is used because it does not, like free dinitrophenol, act upon the iron vessels in which the timber is impregnated; it is also active as an antiseptic. The selective phenomena observed when treating timber with mixtures of zinc fluoride and hydrochloric acid are reproduced in the "Bellit" treatment.

CHROME-NICKEL BRONZE.

Chrome-nickel bronze is now being manufactured by a Philadelphia company, the product being known as "Chromax Bronze." The proportions of metal in the alloy are said to be as follows: Copper, 66.66 per cent.; zinc, 12.13 per cent.; nickel, 15.15 per cent.; chromium, 3.03 per cent.; and aluminum, 3.03 per cent. The tensile strength of the alloy is said to be 79,000 lbs. per sq. in.; the color is white, and it takes a fine, silvery polish; the fracture is fine and dense, particularly after being remelted; and the alloy, owing to its high melting point, has a denser structure and greater compressive strength than manganese bronze. It can be rolled into sheets and wire.

NOTES AND CORRESPONDENCE

NOTES ON THE COMPOSITION AND ANALYSIS OF DESICCATED MILK AND CREAM.

By R. S. Fleming.

The analysis of desiccated milk presents several difficulties which do not appear in the analysis of fresh liquid milk, and serious errors have been made through assuming that methods which apply to the one would necessarily apply to the other. Especially is this the case in the estimation of butter fat.

Before making the analysis the sample should be thoroughly mixed and then placed in a tightly stoppered bottle to prevent the absorption of moisture, most milk powders being quite hygroscopic.

Moisture is estimated by drying in a wide shallow weighing bottle one or two grams of milk powder to constant weight, preferably in a vacuum oven at 95° to 100° C. Five hours is generally sufficient. Do not dry longer than this without weighing. A slight increase in weight takes place after long drying, probably from oxidation of some of the constituents. In the absence of a vacuum oven an ordinary water or steam oven having a temperature of 99° to 100° would give fair results, but it takes considerably longer, about 10 hours, and even then the results are likely to be a trifle low.

Milk sugar can be best determined gravimetrically as follows: Weigh out in a small beaker 2½ grams of the milk powder or such a quantity that there is not over 0.3 per cent. of sugar in the purified solution. Add a little warm water at about 50° C. and stir up the mixture to a smooth paste, then add more warm water and wash into a 500 cc. flask. Shake up with the warm water until thoroughly dissolved. Small particles of the milk powder are liable to remain undissolved if care is not taken. Cool and make up the volume to about 400 cc. Add 10 cc. to Fehling's copper sulphate solution and proceed as in A. O. A. C. methods, *Bull.* **107,** Bureau of Chemistry, pages 119 and 148. Preferably deposit the reduced copper electrolytically from sulphuric acid solution.

Cane sugar, if present, can be estimated readily by a modification of the Stokes and Bodner method, by which the cane sugar is inverted by means of citric acid, the citric acid having no inverting action on the milk sugar. In a 250 cc. Erlenmeyer flask, place 50 cc. of the sugar solution prepared as for milk sugar determination by precipitating proteins, etc., with copper sulphate and carefully neutralizing. Add 0.5 gram of citric acid. Boil with reflux condenser for 35 minutes. Neutralize and determine the reducing power of the solution in same way as for milk sugar, adding the boiling Fehling solution directly to the flask containing the sugar solution. From the weight of copper found, subtract the amount found in previous determination for the milk sugar, multiply by the factor 0.5395 as given by Allen, Volume 1, page 284. This gives the amount of cane sugar.

Casein is rather difficult to determine from the fact that it precipitates in very fine particles that clog the filter. The following has been found by the writer to be the most satisfactory of several methods tried: To 50 cc. of a 10 per cent. solution of the milk powder at 40° C. add 2 cc. of a warm saturated solution of potassium alum. Allow to settle. Filter on a large filter paper (15 cm.). If the filtrate is not clear, filter on another smaller paper. Transfer precipitate to filter. Wash and place filter papers and contents in a Kjeldahl flask. Determine nitrogen by any of the Kjeldahl modifications. If the Gunning method is used, add a little anhydrous copper sulphate to hasten the reaction. Three hours' digestion by this method is generally sufficient. Use the factor 6.38.

Albumin is approximately determined by subtracting the casein from the total protein. The latter may be determined by digesting one gram of milk powder and proceeding in the regular way. It is to be noted that in milks which have been highly heated the albumin is partially or wholly coagulated. In that case the suspended albumin will precipitate with the casein, making the percentage of the latter higher than it should be.

Ash is best determined by incinerating one or two grams in a platinum dish at a low red heat. For the first half hour use a very low flame.

Butter fat may be determined by any of the following methods:

First. Extraction with pure ethyl ether of a specific gravity of 0.720 (anhydrous ether + 0.5 per cent. by volume of water) as described by McLellan, *Analyst*, **1908,** page 353. It is unnecessary, however, to soak over night and re-extract. Sixteen hours' continuous extraction in a Soxhlet or a direct extraction apparatus is sufficient. Schleicher & Schuell's double thick extraction cartridges are excellent for retaining the fine particles of milk powder.

Second. The Werner-Schmidt method. This method is most conveniently applied as follows: Weigh out one gram of milk powder. Place on a well annealed glass stoppered tube of at least 80 cc. capacity. Add 5 cc. of water. Shake until homogeneous, then add 7.5 cc. of concentrated hydrochloric acid (sp. gr. 1.19). Shake until dissolved. Remove the stopper. Place in boiling water bath for five minutes, shaking gently to keep the mixture agitated. Remove and cool. Then add pure ethyl ether. Shake vigorously, allow to settle for ten minutes. Remove ethereal layer to a weighed flask by means of a wash bottle connection. Repeat the extraction three times. Evaporate off the ether and dry in the water oven. Cool and weigh. Should the fat be contaminated, as it will be at times, dissolve out the fat with petroleum ether, leaving the impurities adhering to the flask. Dry and re-weigh. Subtract the impurities.

Third. A new method worked out by Redmond in this laboratory and described in the accompanying paper, "A New Method for the Determination of Fat in Desiccated Milk," has been found to give splendid results.

Fourth. The Rose-Gottlieb method has been found to give satisfactory results, but is somewhat tedious.

The following methods have been found to be unsatisfactory as they give low results: Adams, Babcock, extraction with anhydrous ether or chloroform.

The *composition* of milk powder varies within wide limits. Very recently cream powder has been put on the market which has almost as high a butter fat content as butter itself. Small amounts of cane sugar are frequently added. Modified milk for infants has much less casein, more albumin and more milk sugar than normal milk. The accompanying table gives the analyses of a number of different milk and cream powders:

No.	Butter fat.	Casein.	Albumin.	Milk sugar.	Cane sugar.	Ash.	Moisture.	Total.
1	29.12	24.06	1.86	37.52		5.72	1.48	99.76
2	1.81	32.31	5.85	49.32		8.21	2.53	100.03
3	15.26	27.18	4.84	43.92		6.46	2.03	99.69
4	0.6	2.3	10.20	77.2		9.10	1.40	100.80
5	11.25	11.30	7.57	60.10		7.66	1.37	99.25
6	53.08	16.89		26.04		3.78	0.81	100.60
7	67.64	12.21		15.92		2.67	0.76	99.20
8	21.00	18.90		23.82	29.98	3.93	2.94	100.57
9				47.16	2.25			
10				49.71	1.54			

No. 1, made from whole milk.
No. 2, made from skimmed milk.
No. 3, made from half skimmed and half whole.
No. 4, made from whey, the casein having been largely removed.

No. 5, made from whole milk modified with whey. When dissolved with the proper proportion of water it has approximately the composition of human milk.

No. 6, made from light cream and No. 7 from heavier cream.

Nos. 1 to 4, made from known milks.

No. 8, evidently from whole milk with the addition of cane sugar.

No. 9 and No. 10, evidently from skimmed milk with the addition of small amounts of cane sugar.

Nos. 8, 10 made from unknown milks.

LABORATORY, MERRELL-SOULE CO.,
SYRACUSE, N. Y., Feb. 17, 1912.

A MODIFICATION OF THE BABCOCK TEST AS APPLIED TO THE ESTIMATION OF FAT IN DESICCATED MILK.

By N. GREGORY REDMOND.

As the Babcock method is the one most generally used by dairymen and manufacturers using milk products, either it or some equally unsuitable method is often applied to determine the fat in desiccated milk. Van Slyke[1] appreciates the fact that the ordinary Babcock method, when used with milk powder, gives results which are too low.

It occurred to the writer that it would be an advantage if the Babcock test could be so modified that it would give accurate results. This modification was finally worked out, and has been successfully used for several months. To test the accuracy of the method, the fat was determined on a sample of desiccated milk by several different methods. One of those used was the Werner-Schmidt method. That this method is trustworthy has been shown by H. D. Richmond[2] and also by an abstract in *The Analyst* of a recent paper by A. Burr[3] on the "Composition of Dried Milk Powder." The results which are shown in the table prove that the direct extraction of the milk powder with anhydrous ether gives results which are too low. In each case where a direct extraction was made, the powder was first dried at 90° C. to 100° C. for at least five hours. In using the Werner-Schmidt method the fat was redissolved in petroleum ether and an allowance made for any impurities. This was also done with the direct extractions when the fat appeared to be impure.

In the ordinary Babcock test, the powder was weighed and transferred to the test bottle, then dissolved in warm water, cooled, and concentrated sulphuric acid added. This prevents any error which might occur from inaccurate sampling by measuring an aliquot part of a 10 per cent. or 20 per cent. solution. The general experience of this laboratory has been that this method is about 3 per cent. low.

The accuracy of the new method is shown by the fact that the average of ten determinations by the various methods (excluding the direct extraction with ether distilled over sodium and the ordinary Babcock method) is 28.49 per cent. fat, and the average of four determinations by the new method is 28.62 per cent. fat.

A determination in duplicate by the new method can easily be made in less than one hour. Some of its advantages are cheapness, simplicity, speed and accuracy.

The following is a description of the method:

Weigh 2.5 grams of milk powder and transfer it to an ordinary Babcock milk bottle, graduated to 10 per cent. A glass funnel (about 2″ in diameter and with the stem cut off to ½″) is inserted in the neck of the bottle and is of great help in transferring the powder. Add 31 cc. of dilute sulphuric acid (395 cc. concentrated H_2SO_4 diluted to 1 liter) and place the bottle upright in a dish of gently boiling water. Shake frequently and keep in the boiling water until all the powder is dissolved and the solution is dark brown in color. This usually takes from 7 to 10 minutes. After removing the bottle from the water add 12 cc. concentrated H_2SO_4 (sp. gr. 1.82–1.83) and mix thoroughly, taking care to keep the solution out of the neck of the bottle. Agitate with a rotary motion. Place the bottle in a centrifuge and whirl for 4 or 5 minutes. Add hot water until the solution reaches the lower end of the neck, whirl again for 1 minute, then add hot water until the fat rises. Whirl again for 1 minute. In order to secure accurate results, the fat column must be read at a temperature not above 140° F. nor below 130° F; by setting the bottle in water, the desired temperature may be reached. Readings should be made to 0.05 on the bottle. The reading multiplied by 7.2 gives the percentage of fat.

2.5 grams : 18 grams = Reading : X.

If reading = 4.00, then 2.5 : 18 = 4.00 : X.

$$\text{Or } X = 4.00 \times \frac{18}{2.5} = 4.00 \times 7.2 \text{ or } X = 28.80 \text{ per cent.}$$

A COMPARISON OF DIFFERENT METHODS OF DETERMINING FAT IN MILK POWDER.

	Fat. Per cent.	Averages.
Squibb's ether—16 hours' direct extraction	28.30 28.45	28.37
Ether containing 5 cc. H_2O per liter, 16 hours' direct extraction	28.50 28.55	28.52
Ether containing 5 cc. H_2O per liter, 18 hours' direct extraction	28.50 28.60	28.55
Ether containing 5 cc. H_2O per liter, Werner-Schmidt method	28.50 28.56	28.53
Anhydrous ether (distilled over sodium), Werner-Schmidt method	28.39 28.54	28.46
Average of ten determinations above		28.49
By the proposed new method	28.80 28.44 28.44 28.80	28.62
Anhydrous ether (distilled over sodium), 16 hours' direct extraction	13.55 13.40	13.47
Babcock method	25.20 25.20	25.20

Babcock bottles vary in volume. It is more convenient to use bottles which hold at least 45 cc. of water when filled to the lower end of the neck. The bottle should be thoroughly cleaned, rinsed with alcohol and dried (to prevent powder sticking in the neck) before using. This insures clear and accurate readings. Commercial sulphuric acid has been used in making the dilute H_2SO_4 solution and good results were obtained. It is better, however, to use c. p. acid and thus avoid contamination of the fat column by impurities in the acid.

LABORATORY, MERRELL-SOULE CO.,
SYRACUSE, N. Y., Feb. 17, 1912.

[1] "Modern Methods of Testing Milk and Milk Products," **1906**, Ed., p. 86.

[2] *The Analyst*, **31**, No. 364, pp. 218–224.

[3] *Ibid.*, **36**, No. 423, p. 279.

ALUNDUM NOT CONSTANT IN WEIGHT.

By E. B. FORBES.

The invention of porous earthenware laboratory utensils immediately satisfied a large number of urgent and long-standing requirements. As is inevitable under such circumstances this new ware has been put to some uses which it is not adapted to serve, and a correct appreciation of its very great value in the laboratory requires that we search out and recognize its limitations.

In an effort to shorten and improve upon the usual method for crude fiber determination, we followed the Morgan P. Sweeney modification except that instead of straining through an unstandardized cloth we conducted our filtration, washing and ignition all without transfer, in an alundum extraction capsule. It appeared to be a beautiful method, and through the substitution of an efficient, standardized filter for the rag strainer it seemed to remove from this very unscientific determination one of the principal grounds for our objections; but things were not as they seemed. Alundum is not constant in weight through treatment with water and heat.

TABLE I.—EFFECTS OF HEAT AND WATER ON WEIGHT OF ALUNDUM.

Capsule No.	Wt. after washing with water and drying 2 hrs. at 100°. Grams.	Wt. after ignition in muffle. Grams.	Change in wt. during ignition. Mg.	Wt. after washing with water and drying 3 hrs. at 100°. Grams.	Wt. after washing with water and drying 2 hrs. more at 100°. Grams.	Wt. after ignition in muffle. Grams.	Change in wt. during ignition. Mg.	Wt. after 2nd ignition compared with wt. after 1st ignition. Mg.
1	11.3179	11.3136	—4.3	11.3180	11.3180	11.3146	—3.4	+1.0
2	13.1128	13.1098	—3.0	13.1130	13.1130	13.1108	—2.2	+1.0
3	13.0326	13.0292	—3.4	13.0326	12.0326	13.0310	—1.6	+1.8
4	11.5042	11.5014	—2.8	11.5044	11.5044	11.5032	—1.2	+1.8

Table I sets forth results of a test with four alundum extraction capsules. They were washed with water, dried at 100° for 2 hours, weighed, burned in a muffle and weighed again. In all weighings the capsules were contained in glass weighing bottles where they had been placed while as hot as they could be without breaking the glass. The weighing bottles were dried with the capsules in the oven and were kept in desiccators over sulphuric acid.

The weight after firing showed that all of the capsules had lost in weight, the amounts varying from 2.8–4.3 mg. Perhaps they were not dry. We then washed with water and lengthened the drying to 3 hours at 100°, weighed, dried 2 hours more at 100° and weighed again. There was no change in weight between dryings, but when fired all lost in weight from 1.2–3.4 mg.; and what is more, the capsules did not return to the weight obtained after the first firing but during this second test gained 1.0–1.8 mg.

TABLE II.—EFFECTS OF HEAT AND WATER ON WEIGHT OF ALUNDUM.

Capsule No.	Wt. after washing with water and drying 3 hrs. at 110°. Grams.	Wt. after drying 3 hrs. at 120°. Grams.	Wt. after ignition in muffle. Grams.	Change in wt. during ignition. Mg.	Wt. after washing with water and drying 3½ hrs. at 160°. Grams.	Wt. after ignition in muffle. Grams.	Change in wt. during ignition. Mg.	Wt. after 2nd ignition compared with wt. after 1st ignition. Mg.
1	11.3160	11.3160	11.3138	—2.2	11.3164	11.3136	—2.8	—0.2
2	13.1128	13.1128	13.1102	—2.6	13.1116	13.1096	—2.0	—0.6
3	13.0326	13.0326	13.0309	—1.7	13.0340	13.0306	—3.4	—0.3
4	11.5044	11.5044	11.5026	—1.8	11.5036	11.4996	—4.0	—3.0
5	10.2566	10.2566	10.2544	—2.2	10.2566	10.2530	—3.6	—1.4
6	13.4062	13.4062	13.4040	—2.2	13.4066	13.4028	—3.8	—1.2
7	11.7162	11.7162	11.7146	—1.6	11.7166	11.7142	—2.4	—0.4
8	10.8086	10.8086	10.8070	—1.6	10.8092	10.8060	—3.2	—1.0

We then added four more capsules to the test (Table II), washed with water, dried for 3 hours at 110°, weighed, dried for three more hours at 120°, weighed, fired and weighed again. Between dryings the weights were absolutely constant, but on firing we got a loss of 1.6–2.6 mg.

Next we washed in water, dried for 3½ hours at 160°, weighed, ignited and weighed. This time there was as before a loss in each case from 2.0–4.0 mg. and this last weight as compared with the one after the previous ignition showed in each case an appreciable loss.

TABLE III.—EFFECTS OF HEAT ON WEIGHT OF ALUNDUM.

Capsule No.	Wt. after last previous ignition. Grams.	Ignited and weighed. Grams.	Change in wt. during ignition. Mg.	Ignited and weighed again. Grams.	Change in wt. during ignition. Mg.	Ignited and weighed again. Grams.	Change in wt. during ignition. Mg.
1	11.3136	11.3142	+0.6	11.3174	+3.2	11.3172	—0.2
2	13.1096	13.1110	+1.4	13.1144	+3.4	13.1140	—0.4
3	13.0306	13.0312	+0.6	13.0354	+4.2	13.0350	—0.4
4	11.4996	11.5008	+1.2	11.5046	+3.8	11.5038	—0.8
5	10.2530	10.2538	+0.8	10.2564	+2.6	10.2566	+0.2
6	13.4028	13.4043	+1.5	13.4082	+3.9	13.4078	—0.4
7	11.7142	11.7144	+0.2	11.7180	+3.6	11.7178	—0.2
8	10.8060	10.8064	+0.4	10.8101	+3.7	10.8095	—0.6

One point had become clear. Water combines chemically with some constituent of the alundum capsule, a combination which is not broken up at 160° but which is destroyed at a temperature considerably below 1000°.

To throw more light on the apparent change in the weight of the capsule aside from that caused by the hydrating and dehydrating process above referred to, we subjected the same eight capsules to three consecutive firings and weighings without treatment with water. The weights are set down in Table III. In the first firing the capsules gained 0.2–1.5 mg., in the second from 2.6–4.2 mg. more, and in the third firing one capsule gained 0.2 mg. while the rest lost 0.2–0.8 mg.

Thus aside from the change in weight due to the taking up and loss of water there seems to have been operative a second factor resulting in a gain in weight which partially compensated for the losses occasioned as above mentioned, this gain not reaching its limit, under conditions existing in the muffle, until the second firing after the tests reported in Tables I and II. The reddish yellow color of the alundum became much lighter during these tests, perhaps due to change in the condition of the 0.5 per cent. of iron contained therein.

OHIO AGRICULTURAL EXPERIMENT STATION,
February 19, 1912.

THE CENTENARY OF THE INTRODUCTION OF GAS.

The Centenary of the Introduction of Gas was celebrated in Philadelphia on Thursday and Friday, April 18th and 19th, according to the program published in the April issue of THIS JOURNAL, p. 309.

The addresses are now appearing in full in the *American Gas Light Journal* and in the *Proceedings of the American Gas Institute*. A limited edition is also being printed in book form; 180 pages, illustrated. Price, $2.00. Copies should be ordered at once of the American Gas Institute, 29 West 39th St., New York City.

Brief abstracts of the five addresses follow:

By-Products in Gas Manufacture. By CHARLES E. MUNROE, Professor of Chemistry at George Washington University.

Professor Munroe's address gave an excellent review of the scope and influence of the gas industry since it took up not only the real by-products of gas manufacture, but the subsidiary products which are often those of allied industries.

Among the subsidiary products were mentioned dyes, explosives, flavoring materials, perfumes, synthetic drugs, sweetening principles and photographic developers—all obtained from the by-product, coal-tar, while water-gas tar yields light oils of the benzole series, creosoting oils, naphthalene oils, road compounds and pitches.

The U. S. Bureau of Mines has taken up the study of the entirely unknown constitution of coals in connection with the work they are doing toward the more complete and economic development of our fuel resources.

The by-products of the coal gas industry are coke, gas, carbon, tar, ammoniacal liquor and spent purifying material, either lime or oxide: in the water gas industry, tar and purifying material with a meager amount of ammoniacal liquor: in the oil gas industry, lampblack, tar and spent purifying material for the new Low process, and "hydrocarbons" for the cracked and compressed oil gases. In the acetylene gas industry calcium hydroxide is practically the only product incidental to the reaction other than the acetylene.

The importance of the many varieties of nitrogen and ammoniacal products to the fertilizer industry as well as to the nation were presented with care, as well as the methods for their

preparation, special attention being given to the processes for ammonia recovery.

Finally the speaker's scheme of producing gas at the coal mine and shipping it by pipe line was discussed, and it was noted that Sir Wm. Ramsay had recently given this suggestion his endorsement.

The Commercial and Financial Aspects of the Gas Industry. By GEORGE B. CORTELYOU, President of the Consolidated Gas Company of New York.

A portion of this address was devoted to a historical account of the development of the gas industry together with a discussion of the objections raised to the introduction of gas.

The ever-increasing output of gas, notwithstanding the competition from electricity, kerosene lamps, etc., has been accompanied by a steadily diminishing price of gas. Sales of gas in large cities grow almost twice as fast as the population. In view of this fact, the speaker predicted a steady growth of the gas business, if properly operated, with constant provision for invention and improvement. The importance of scientific salesmanship, combined with efficient and prompt service, was strongly emphasized.

The speaker discussed the relations of employees to the company and the public; franchises, municipal and private ownership; competition *vs.* monopolistic control of Public Utilities; and Commission Regulation.

The Technic of Gas Manufacture. By ALFRED E. FORSTALL, Secretary Trustees Gas Educational Fund of the American Gas Institute.

Being unable to find a description of manufacturing apparatus specifically stated to have been used in the first works of the Chartered Gas Light & Coke Company, the speaker told of the apparatus described by Accum in 1815. This was followed by a detailed account of the modern coal gas plant, the various improvements being noted in order.

The fact that more than two-thirds of the total amount of illuminating gas made and sold in this country is carburetted water gas, called for a description of its methods of manufacture. Brief mention was made of the California process, the use of wood gas and of "Mond gas."

Especial attention was called to the many factors which enter into the control of gaseous products and by-products due to the complex nature of the raw materials, final products and the reactions that take place in the process of manufacture.

Gas as an Illuminant. By VAN RENSSELAER LANSINGH, President of the Illuminating Engineering Society, New York.

After a discussion of lighting by torches, candles, oil lamps and kerosene lamps, the speaker took up gas lighting, beginning with Murdock's burner which was merely a small iron tube open at the end. This was succeeded by the bats-wing, the fish tail, the Argand and the regenerative burners.

The invention of mantle burners by Auer von Welsbach in 1885 made modern gas lighting possible.

Flat flame burners are now used only in special instances and no reliance can be put in the consumption rating of these burner tips on the American market.

Much poor gas service can be traced to failure to select mantle burners adapted to the existing quality of gas and pressure conditions. With ordinary shades, flat flame burners give spherical distribution of light, upright incandescents give two-thirds of their light above, and inverted burners two-thirds below horizontal. High pressure increases the candle power of mantle burners as much as two and one-half times and is used chiefly in street lamps. With increased candle power, diffusion becomes more and more necessary so that bare mantle burners are rare.

Methods of gas ignition were merely noted.

The speaker recommended greater range in size of units, reliable methods of commercially rating lamps and standardization of mantles, lamps, and fittings.

The Use of Gas for Heat and Power; The Testing of Gas. By MR. E. B. ROSA, Chief Physicist, Bureau of Standards, Washington, D. C.

With more than 1300 gas companies in the country, with a combined capital of one billion dollars and annual sales of two hundred million dollars, the gas industry is indeed an important one.

Mr. Rosa discussed the use of coal, acetylene, natural and producer gases, and the historical development of the use of gas for cooking, water heating, room heating and industrial purposes. This was followed by a brief resumé of the work that has been done on the various types of gas engines.

Thanks were extended on the part of the Bureau of Standards to the officers and technical staffs of the various gas companies and to the members of public service commissions, gas inspectors and consulting engineers for the fairness and broad-minded spirit they have shown in discussing the questions connected with the work now being done by the Bureau towards the standardization of the testing of gas.

The work accomplished already was discussed and special stress was laid on the necessity for using the *net heat* for measurement of the heating value of a gas. The effect of atmospheric conditions on the gross heat was shown and it was suggested that a committee of the American Gas Institute coöperate with the Bureau in studying the question *"Shall the actual net heat be substituted for the gross?"* Mr. Rosa believes that since instruments and methods of measurement are more accurate than ever before, uniform standards of gas quality should be adopted, taking into account varying density as well as accurate measurements of volume and quality. The next publication of the Bureau will take up these questions of testing methods, and the cordial coöperation of the gas interests is earnestly solicited.

AMERICAN ELECTROCHEMICAL SOCIETY RESEARCH FUND.

In order to further the objects of our Society as given by our Constitution, it has seemed wise to try the experiment of assisting purely scientific research work in electrochemistry where this is done under conditions which would make the application of a few hundred dollars annually of effective and efficient assistance.

For this purpose, $250 is made available for this year, to be given in whole or in part to help members of the Society who need such assistance to carry on some predetermined work.

The Committee does not wish to burden the scheme with unnecessary rules or requirements, and proposes to carefully consider requests for this assistance on the merits of the case as it may be presented. If the further developments of the scheme warrant the issuing of limitations on the distribution of the fund, such will be published.

The Committee's aim will be to give assistance to those who are apparently equipped to do effective work along those purely scientific lines which are not usually explored by commercial or industrial organizations. In other words, we wish to advance the science of electrochemistry.

The research work thus assisted must be published in the Transactions of the Society.

Applications may be sent to the Chairman of the Committee and should be received before August first.

W. R. WHITNEY, *Chairman*,
W. H. WALKER,
F. A. J. FITZGERALD.

MAINE SECTION OF THE AMERICAN CHEMICAL SOCIETY.

The recently authorized Maine Section of the American Chemical Society held its initial meeting in Fernald Hall on the University of Maine Campus on May 16, 1912. The meeting was attended by about thirty enthusiastic members of the

Section and at the afternoon meeting, at which papers were presented, there were present a number of student chemists of the University of Maine. Papers were presented by Mr. A. B. Larchar, of Oldtown, on "Some Practical Observations on the Electrolysis of Brine;" by R. H. McKee on "An Oil from the Red Spruce;" and by L. M. Burghart on "Some New Forms of Chemical Apparatus."

After discussion the meeting temporarily adjourned to give opportunity for the preparation of a lunch which was served in the laboratory. After lunch a short business meeting was called to order by R. H. McKee and a committee nominated the following officers who were elected to serve until organization has been perfected and by-laws adopted: *President of the Section*, A. B. Larchar, Oldtown; *Councilor*, R. H. McKee, Orono; *Secretary and Treasurer*, H. H. Hanson, Orono. The officers named were elected as an executive committee to arrange for the next meeting and to present at that meeting by-laws to govern the Section. H. HANSON, *Secretary*.

ORGANIZATION OF COMMITTEES FOR STUDY OF INDUSTRIAL DISEASES.

The membership of the Committee on Industrial Diseases of the New York Association for Labor Legislation is made up of the following:

PROF. HENRY R. SEAGER, President of the American Association for Labor Legislation, *Chairman*.

PROF. SAMUEL McCUNE LINDSAY, President New York Association for Labor Legislation, *Ex Officio*.

DR. CHARLES L. DANA, Chairman Committee Public Hygiene, Academy of Medicine, *Ex Officio*.

DR. JOHN B. ANDREWS, Secretary American Association Labor Legislation.

CHAS. BASKERVILLE, Professor of Chemistry, College of the City of New York.

DR. WARREN COLEMAN, New York Academy Medicine.

MR. MILES M. DAWSON, Actuary.

MR. LEONARD W. HATCH, Statistician Department Labor, State of New York.

MR. FREDERICK L. HOFFMAN, Statistician Prudential Life Insurance Co.

DR. JOHN H. HUDDLESTON, New York Academy Medicine.

DR. JAMES ALEX. MILLER, New York Academy Medicine.

DR. W. GILMAN THOMPSON, New York Academy Medicine.

DR. LINSLY R. WILLIAMS, New York Academy Medicine.

PROF. C. E.-A. WINSLOW, College of the City of New York.

MR. PAUL KENNADAY, Secretary New York Association Labor Legislation.

The Committee on Occupational Diseases in Chemical Trades, New York Section of the American Chemical Society, is as follows:

DR. GEO. P. ADAMSON, Baker & Adamson Chemical Co., Easton, Pa.

MR. W. H. BASSETT, American Brass Co., Waterbury, Conn.

MR. WM. F. DOERFLINGER, Mutual Chemical Co. of America, 55 John St., New York City.

DR. A. C. LANGMUIR, Chairman New York Section, 9 Van Brunt St., Brooklyn, N. Y.

DR. GEO. D. ROSENGARTEN, Powers, Weightman & Rosengarten, Philadelphia, Pa.

DR. A. H. SABIN, National Lead Co., 129 York St., Brooklyn, N. Y.

MR. E. C. UHLIG, *Secretary*, Brooklyn Union Gas Co., 5th & Hoyt Sts., Brooklyn, N. Y.

ORGANIZATION OF RUBBER SECTION.

Editor of the Journal of Industrial and Engineering Chemistry:

At a meeting of the Rubber Section of the American Chemical Society held on June 5th, the following committees were appointed:

General Rubber Consideration Committee: D. A. Cutler, *Chairman*; H. van der Linde, W. E. Piper, G. T. Cottle, A. D. Hopkins, D. Spence, Dorris Whipple, C. R. Boggs, H. Fay, W. C. Geer.

Analytical Committee: Dorris Whipple, *Chairman*; J. W. Schade, P. H. Walker, J. B. Tuttle, G. T. Cottle, Geo. Oenslager, W. A. Ducca.

Committee on Specifications: C. R. Boggs, *Chairman*; G. H. Savage, H. Fay, W. C. Geer, H. B. Rodman, D. A. Cutler.

It was also decided to have the General Rubber Consideration Committee ask all the members of the Section to submit the best known method for analyzing rubber goods; the Committee is then to select the best method, submitting same to the American Chemical Society asking the Society to publish this as being the best authority known to it at the present time. The Analytical Committee will, in the meantime and in the future, attempt, by research and such other methods as it may select, to revise this adopted method from time to time, as may seem best for the interests of the Rubber Section, the object being that any chemist in the country who may have occasion to analyze rubber goods may have an authorized standard method of procedure.

When this has been accomplished there should not be such a variance in the results reported from different chemists who analyze vulcanized rubber products. We hope to have this accomplished so that it may be announced at the coming International Conference in September.

D. A. CUTLER, *Chairman*.

PAINT AND VARNISH IN THE U. S. NAVY.

Editor of the Journal of Industrial and Engineering Chemistry:

I notice in your issue of May, 1912, a communication from Professor Sabin, in which he refers to the steps taken recently by the Naval authorities looking toward the use of so-called "newer paint materials."

Professor Sabin seems to be under the impression that the Navy Department expects to find these materials not so efficient as those previously used, and that they are even willing that such should be the case.

As I have been identified, to some extent, with literature on this subject, and a good deal of prominence has been given to a paper which I presented to the Naval Institute in December last, I feel that I should attempt to correct the impression given by Professor Sabin in his letter.

Although one of the arguments advanced in favor of the use of cheaper paint materials was to the general effect that even if they were not quite so lasting, there would be still ample reason for their use in view of the frequent repainting that is necessary from other considerations, the use, however, of materials that are less effective than those heretofore used actually has not been accepted and all of the changes that have been made by the Navy Department have been made only after extensive experiments showed that there would be no loss in efficiency. The changes to date have been the use to some extent of lower priced and more effective paints in place of red lead as a priming coat, the use of hydrocarbon spirits in place of turpentine, the use of blanc fixe in slate colored outside paint for battleships and cruisers, and the tentative use of fish oil in place of a portion of the linseed oil. These changes were not made, however, until, as noted above, the naval authorities were convinced that there would be no loss of efficiency in durability of the paints or in protective effect. HENRY WILLIAMS.

NAVY YARD, NEW YORK.

A COLORIMETRIC METHOD FOR THE DETERMINATION OF CARBON IN IRON AND STEEL. A NOTE OF PROTEST.

The Editor of the Journal of Industrial and Engineering Chemistry:

In the May number of THIS JOURNAL, there is, under the title "A Colorimetric Method of Determining Carbon in Iron and

Steel," what purports to be a "novel" method of determining carbon by a modification of the Eggertz process; as this "new" method has probably been practiced ever since the Eggertz process was introduced, I think it is time a protest was entered against such self-evident modifications being published as original. I do not know to whom this particular method of dilution is originally due, but it has been used by nearly all steel works chemists in this country for the past 17 or 18 years to my personal knowledge.

A modification of the Eggertz process which I do not know to be so commonly used, as it might well be, refers to the determination of carbon in very soft steel, etc., and when the carbon is below 0.10%, is carried out by weighing a portion of a standard steel, say 0.1 gram, and adding 0.1 gram of the sample to it; this is dissolved alongside a 0.2 gram portion of the same (or other) standard and the two compared, when a simple calculation will give the result for the steel.

Any one who is associated with the comparison of low carbon steels, *i. e.*, steel with carbon under about 0.10 per cent., will be acquainted with the difficulty of comparison on account of the greenish tint; the above process is designed to overcome this difficulty and I can confidently recommend its trial.

While on the subject of carbon determination, I might mention that I have successfully used a similar process in connection with the determination of carbon by direct combustion in oxygen of the more refractory ferro alloys: by placing a known quantity of a standard steel in the combustion boat and sprinkling the weighed portion of the alloy over this, when the heat generated by the combustion of the steel standard has been sufficient to insure complete combustion of the alloy.

I am not claiming originality for these modifications which are in this country looked upon merely as "shop kinks."

E. ESCOTT WOOD.

LABORATORY OF THE BRYMBO STEEL WORKS,
WREXHAM, WALES.

A COLORIMETRIC METHOD FOR THE DETERMINATION OF CARBON IN IRON AND STEEL—A NOTE.

Editor of the Journal of Industrial and Engineering Chemistry:

In the May issue of THIS JOURNAL for the current year there appeared an article entitled "A Colorimetric Method for the Determination of Carbon in Iron and Steel." This method is claimed to be similar to the one proposed by Eggertz. This statement was very surprising to me because I had studied Eggertz' method under him in the Royal Mining School at Stockholm, Sweden, and later, in my own laboratory, I made about five thousand determinations using his method. When reading Mr. Kohout's method, I found same identical with Prof. Eggertz' method. At present I can only refer to a foot-note in Blair, "Analyses of Iron and Steel" on page 170, 5th edition, and page 175, concerning the dilution of the standard.

Yours very truly,

C. G. HELLMAN.

165 GRAND STREET,
JERSEY CITY, N. J.

VALUATION OF FLUORSPAR—A CORRECTION.

In my article in this paper, Vol. 4, No. 3, March, 1912, I quoted incorrectly Mr. F. Julius Fohs' statement published in *Bulletin* 9 of the Kentucky Geological Survey, *viz.*, "silicates occurring associated with Kentucky fluorspar." The word "Kentucky" should be omitted: it disturbs the meaning of the following discussion, changing the same to a depreciative criticism of Mr. Fohs' statement, which I did not intend to do. Mr. Fohs states that the silicates mentioned in my article occur occasionally associated with fluorspar, but not with Kentucky fluorspar.

ERNST BIDTEL.

GENERAL BAKELITE COMPANY STARTS INFRINGEMENT SUITS.

General Bakelite Company has brought suits for infringements of its Bakelite patents against the Condensite Company of America and several users of "Condensite;" among them the Dickinson Manufacturing Co. of Springfield, Mass., The Duranoid Mfg. Co. of Newark, N. J., and Hardman & Wright of Belleville, N. J.

In relation to this, it is of interest to note that the fundamental Bakelite patents have been allowed in Germany and have been sustained by the German Patent Office, notwithstanding the fact of several public contestations.

THE END OF THE COÖPERATIVE GLASS FACTORIES IN ITALY.

In the "Fachgenosse", 28, No. 58 (an organ of the German glass unions), appears an article noting the failure of the coöperative glass factories of Italy in their struggle with the trust (cf. *C. A.*, 5, 166).

These rival glass factories were started by the labor unions in 1903 with the small capital of $5,750. They proceeded to compete with the trusts for the control of the market, hoping at least to compel recognition of their union and improve conditions for the men. During the last nine years these factories have been increased to seven in number at the time of the bankruptcy. Business conditions in the Italian glass industry throughout the last year particularly have been very unfavorable. In 1910 occurred a shortage in the grape crop result in a lessened demand for bottles, and the Turko-Italian war proved to be the last straw in the situation for the coöperative factories. They were scattered over the northern part of Italy, with the exception of one factory in the vicinity of Naples, and with their scanty capital and lack of close coöperation were unable to cope with the hard times and consequent losses.

J. B. PATCH.

INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY. ANNOUNCEMENT BY SECTION I, ANALYTICAL CHEMISTRY.

The President of Section I, Analytical Chemistry of the approaching Congress of Applied Chemistry, desires to call the attention of chemists to an official notification received by him, that two important propositions will be advocated at the Congress.

It will be moved by the Verein deutscher Chemiker: To adopt for practical purposes an atomic weight table only once in five years and on a given date to introduce this generally and recognize it as binding in mutual dealings.

The Sectional Group, "Analytical Chemistry," of the Verein deutscher Chemiker will make the following suggestion: To request the Sub-committee on Uniform Sampling of the International Committee on Analyses to take up the sampling of ores.

For fuller details, consult *Chemiker Zeitung*, June 6, page 635, and *Zeitschrift für angewandte Chemie*, June 7, page 1171.

BOOK REVIEWS

Corrosion of Iron and Steel. By J. NEWTON FRIEND, PH.D. Longmans, Green & Co., 1911. pp. 300; 62 figures. Price, $1.80 net.

With the exception of an occasional failure due to so-called fatigue, the life of a structure made from iron or steel is in general determined by the rate at which it corrodes, or as we say rusts. A voluminous literature of the past exists, while that of the present is constantly being swollen by contributions from the many investigators now in the field. We therefore welcome heartily a book such as the one here considered which so carefully digests the work already reported and collates in such a clear, unbiased way that portion of the literature which seems to be worthy of consideration. The subject is one of immense practical importance, and no engineer or metallurgist can afford to be ignorant of either the purely scientific aspects of the matter, or of those observations which have proved a genuine help in the solution of an apparently simple, but really highly complex problem.

After a brief historical introduction the author discusses what might be called the mechanism of rusting and gives a clear statement of the different theories which have been advanced to explain rusting and the experiments on which such theories are based. He falls into an obvious error, however, when in attempting to distinguish between the so-called acid theory and the electrolytic theory of corrosion, he states that the latter "stands or falls with the solubility or otherwise of iron in perfectly pure water." Elaborate experiments are described which are intended to prove that iron in water in the entire absence of carbonic acid or other electrolyte is not dissolved. What these experiments prove and all that they prove is that under certain conditions below a definite temperature, iron does not dissolve rapidly enough in pure water to be easily noticed. The rate of the reaction increases so rapidly with rise of temperature that it might be expected that if the temperature were raised without changing in any way the other conditions, rusting should become evident; Mr. Fleming in an article in this number of the Journal seems to have proved this to be a fact. But is this all not "using a sledge hammer to kill a flea?" Suppose it were true that at ordinary temperatures iron did not rust in perfectly pure water; this fact in no way invalidates the electrolytic theory. When iron dissolves in water with carbonic acid or without it, energy is set free and can take the form of electrical energy in the same way as that set free by the reaction taking place in a Daniell cell; and the phenomenon is just as truly electrolytic in one case as in the other.

The studied attempt of the author to avoid all the concepts introduced by the electrolytic theory renders the treatment of many important phenomena less clear than it would otherwise be. How else can one explain the accelerating action of metallic platinum or forge scale on the rusting of iron? How explain the protection of iron by zinc, or the fact that the area of iron protected by zinc is a function of the conductivity of the water surrounding the two, and a hundred other facts? To call such phenomena "galvanic action" is simply admitting the facts while refusing to utilize the conclusions which such facts warrant and to use the benefits which may accrue from broader generalizations based upon such facts and conclusions. The book gains nothing by this careful exclusion of the electrolytic theory, while it loses much.

In the chapter devoted to the rusting of iron as influenced by natural forces and conditions the author shows his broad grasp of the literature, and presents the subject in a well balanced discussion of the influence of dissolved oxygen, in water the rate of movement of the water, the action of light, biological activity, etc. To the action of acids, alkalies, aqueous solution of simple salts, and solution of two or more electrolytes on iron there is devoted a chapter respectively. The passive state of iron is the subject of an interesting chapter which brings this interesting subject well up-to-date, as is also true of the section on the influence of the chemical composition of iron on its corrosion. In considering the relative rate of corrosion of iron and steel the author suggests a "Corrosion Factor" and points out that an American firm has made this possible by placing on the market a "pure iron," that is, a metal containing 99.954 per cent. iron. These figures are taken from an analysis given on page 114 as furnished by the American Rolling Mill Co. of Middletown, Ohio, for its product: much to the author's surprise he later found by analyzing the sample himself, that it contained 0.172 per cent. copper.

Throughout the volume, attention is called to the gaps in our present knowledge and its study should prove a source of fruitful suggestion for those looking for subjects for investigation.

The book constitutes a distinct and valuable contribution to the literature on the subject of corrosion, and will prove of interest to the general reader as well as of great service to those particularly interested in the field. WM. H. WALKER.

Technologic Papers of the Bureau of Standards, No. 3: Tests of the Absorptive and Permeable Properties of Portland Cement Mortars and Concretes, together with Tests of Damp-Proofing and Waterproofing Compounds and Materials. By RUDOLPH J. WIG and P. H. BATES. 127 pages, 53 figures; 8vo. Washington: Government Printing Office, 1912.

The investigations reported in this brochure cover some previously unstudied phases of the important subjects of Portland cement mortars and concretes. The account of the work is divided into two parts: Part I comprises the results of a series of tests on 11 different mortars and 23 concretes to ascertain their permeability at various ages, for various consistencies and thickness of test piece, and the absorption on 12 mortars at various ages and for various consistencies, while Part II embodies the results of a series of comparative tests of 40 compounds and several void-filling materials recommended for use or advertised as "damp-proofing" or "waterproofing" mediums, purchased privately in the open market.

Valuable as are the data contained in Part I, the series of tests made on various "damp-proofing" and "waterproofing" compounds and materials should be of more interest to the engineer, architect and contractor—to all those engaged in construction work who have been misled by such statements as, "This compound waterproofs the heart of concrete construction," or "To make the whole mass of the masonry waterproof....add to the cement a compound which is water repellent and breaks up the continuity of the capillaries." It is demonstrated by Wig and Bates, in a quite convincing manner, that Portland cement mortar and concrete can be made practically watertight or impermeable to any hydrostatic head up to 40 feet without the use of any of the so-called "integral" waterproofing materials (19 were tested). Furthermore—but in this case the authors urge cautious interpretation—"The damp-proofing tests as conducted would indicate that Portland cement mortars can be made not only impermeable but damp-proof as well.... without the use of any damp-proofing or waterproofing compound."

There are about fifty waterproofing compounds (coatings and "integrals") on the American market. The addition of "integral" compounds will not, according to Wig and Bates, compensate for lean mixtures, poor materials nor for poor workman-

ships but at least some of the coating compounds have a use, for "As a precaution, under certain conditions, it is undoubtedly desirable to use bituminous or similar coatings, even on new work, as a protection where cracks may occur." However, even in such cases the authors assert that "where cracks can be prevented no coating whatever is required to make the structure impermeable." W. A. HAMOR.

A Dictionary of Applied Chemistry. Second edition, by SIR EDWARD THORPE and other eminent contributors. To be issued in five volumes. Revised and enlarged. Volume I, 758 pages. Price of complete set when issued $50.00. Price per volume, $13.50. Longmans, Green & Co., London and New York, 1912.

The first edition of this well known work appeared twenty-two years ago. In the meantime, great advances have been made in the science of chemistry and its applications, new industries have been developed and established processes have undergone great changes. The appearance of this second completely revised and enlarged edition is therefore a matter of importance to the chemical profession.

The editorial board has been enlarged under the able guidance of Sir Edward Thorpe and now includes forty-five eminent experts selected from England, Germany, Switzerland and America. It would be difficult to find a more representative set of men than those chosen to treat the subjects presented in this volume.

All articles of the first edition have been carefully revised or rewritten and a large amount of new subject matter has been introduced. References to original papers have been more carefully preserved and brought up-to-date. From the standpoint of bibliography alone, the work is of inestimable value and a careful comparison of individual articles shows a consistent and judicious editorial policy.

Volume I covers in its 758 pages, the words A to Che compared with 715 pages in the first edition from A to Dy.

New chapters have been introduced on Abrasives, Acetins, Adhesives, Adrenaline, Amines, Anaesthetics, Argon, Asparagine, Boiler Incrustation, Casein, and a particularly good chapter on Chemical Affinity. These, together with the extention of other subjects which have increased in importance since the first edition, make a book of great reference value to the chemist and chemical engineer.

The general workmanship on the volume is excellent. The paper and binding are well adapted to withstand the hard service of the reference library and laboratory and the chemical profession will receive the timely revision and reissue of this well known work with gratitude to both editors and publishers.

M. C. WHITAKER.

Allen's Commercial Organic Analysis. Fourth Edition, Vol. VI. Edited by W. A. DAVIS and S. S. SADTLER. Philadelphia: P. Blakiston's Son & Co., 1912. Cloth, Octavo viii + 726 pages. Price, $5.00 net

The appearance of this volume, devoted chiefly to the alkaloids and corresponding to Vol. III, Part II, of the previous edition, is especially welcome because of the lack of comprehensive modern literature on the analytical chemistry of the alkaloids. Although 20 years have elapsed since the last edition of this part of Mr. Allen's work, and the material has been entirely rewritten and reset, the scope and general arrangement are but little changed.

As in the other volumes of the fourth edition, the work of revision has been divided among a number of contributors—in this case ten English and four American. The division is as follows: Amines and Ammonium Bases, by W. A. Davis, 49 pages; Aniline and its Allies, by S. S. Sadtler, 60 pages; Naphthylamines, Pyridine, Quinoline and Acridine Bases, by W. H. Glover, 55 pages; Vegetable Alkaloids, by T. A. Henry, 44 pages; Volatile Bases of Vegetable Origin, by F. O. Taylor, 25 pages; Nicotine and Tobacco, by R. W. Tonkin, 18 pages; Aconite Alkaloids, by F. H. Carr, 36 pages; Atropine and its Allies, by F. H. Carr, 28 pages; Cocaine, by S. P. Sadtler, 33 pages; Opium Alkaloids, by F. O. Taylor, 86 pages; Strychnous Alkaloids, by C. E. Vanderkleed, 38 pages; Cinchona Alkaloids, by O. Chick, 72 pages; Berberine and its Associates, by E. Horton, 28 pages; Caffeine, Tea and Coffee, by J. J. Fox and P. J. Sageman, 76 pages; Cocoa and Chocolate, by R. Whymper, 37 pages. Those alkaloids which in the previous edition were included in Part III of Volume III are left for Volume VII of the present edition. Since the work is being entirely reset it seems unfortunate that the descriptions of all the alkaloids should not be brought into one volume.

The division of the subject matter among such a number of contributors has its advantages, as for example in permitting the introduction of a chapter on Cocoa and Chocolate by such a specialist as Mr. Whymper, but it seems also to have resulted in some over-specialization within the volume with a corresponding loss to the more general features. One fails to find in the present volume a satisfactory development of those 33 pages in which 20 years ago Mr. Allen so clearly summarized the general analytical reactions and methods of isolation and purification of the alkaloids as a group.

The separate sections have been extensively rewritten and much new matter included, the volume as a whole being about one-fifth larger than its predecessor. In most sections the descriptive matter is more prominent than the strictly analytical, and the volume will doubtless be used as much for a reference text as for a laboratory guide. H. C. SHERMAN.

The Chemistry of Breadmaking. By JAMES GRANT, M.Sc. TECH., F.I.C., F.C.S. Longmans, Green & Co., 1912. 224 pages, 47 illustrations. Price, $1.25.

This small volume was written to assist the beginner as an introduction to the chemistry of breadmaking. With this purpose in view the author does not attempt to cover the same ground as other more special treatises.

The first 5 chapters of the book take up in a very elementary way the applications of chemistry and physics to the problems of the bakery. Succeeding chapters discuss the composition of cereals and of their milling products, the functions of yeasts and other ferments, breadmaking processes, bakehouse hygiene, fuels and ovens, and the analysis of cereal foods.

As an introductory handbook for students the present volume is in every way much better suited than the more exhaustive work of Jago (THIS JOURNAL, **4**, 313) which is preëminently a book for the specialist and one in which the beginner may have difficulty in finding his way.

The design of Prof. Grant to put forward an introductory volume for beginners which would fill a gap in the literature and text books upon breadmaking is a laudable one and has been very well carried out. C. A. BROWNE.

The Laboratory Apparatus Blue Book, published by the Scientific Materials Co., of Pittsburgh. Sent free of charge to chief chemists, metallurgists and professors.

This book describes and illustrates the apparatus manufactured or imported and sold direct to laboratories by the authors.

A complete list of all the modern and approved laboratory material is given, and arranged alphabetically. The descriptions are clear and a large number, perhaps 2000, different illustrations are used. This catalogue contains a great deal of new and improved apparatus, which will no doubt be of interest to up-to-date chemists.

NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian, Chemists' Club, New York.

Alloy; Metallurgical and Technological Studies in the— Industry. By M. WEIDIG. 8vo. Price, $1.50. Leonhard Simion, Berlin. (German.)

Annual Table of Constants and Numerical Data, Chemical, Physical and Technological for 1910. By CH. MARIE. 4vo., pp. 727. Price, $5.00. University of Chicago Press, Chicago, 1912.

Cellulose; Critical Studies on the Hydrolysis of— and of Wood. By J. NEWMANN. 8vo. Thesis, Technical High School, Dresden (German.)

Cement; Portland— with the Addition of Puzzolan. By S. KASAI. 8vo. Price, $1.25. Tonindustrie Zeitung, Berlin. (German.)

Cerium; The— Metals and their Pyrophoric Alloys. By H. KELLERMANN. L. 8vo., pp. 116. Price, $1.50. W. Knapp, Halle. (German.)

Chemistry; Treatise on General—. (Translation in French.) By W. NERNST. 6th. Edition. 8vo., 422 pp. Price, $2.00. A. Hermann & Fils, Paris.

Coking; Contribution to the Chemistry of—. By F. H. LIERG. 8vo. Price, $.25. Thesis, Technical High School, Dresden. (German.)

Colloid Chemistry. By RICHARD ZSIGMONDY. 8vo. Price, $4.25. Otto Spamer, Leipzig. (German.)

Concrete Costs. By FREDERICK W. TAYLOR AND SANFORD E. THOMPSON. Sm. 8vo., 709 pp. Price, $5.00. John Wiley & Sons, New York.

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Dictionary of Applied Chemistry, Vols. I and II. By EDWARD THORPE. Vol. 5. Revised edition. L. 8vo. Price, $23.00. Longmans Green & Co., London.

Essential Oils: Semi Annual Report of Schimmel & Co., April, 1912. ANONYMOUS. 8vo., 197 pp. Schimmel & Co., Miltitz.

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Organic; Industrial— Chemistry. By SAMUEL P. SADTLER. 4th edition. 8vo., 586 pp. Price, $5.00. J. B. Lippincott Co., Philadelphia.

Potash; The German— Industry. ANONYMOUS. 8vo. Price, $17.00. Mitteldeutsche Privat-Bank, Magdeburg. (German.)

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Radio; The Chemistry of the— Elements. By FREDERICK SODDY. 8vo. Price, $0.75. Longmans, Green & Co., London.

Rubber; The Chemistry of the— Industry. By HAROLD E. POTTS. 8vo., 146 pp. Constable & Co., London.

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Gas; Liquefied Natural—. By WALTER O. SNELLING. *Progressive Age*, Vol. 30, 1912, No. 12, pp. 526–528.

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Tanning; Analysis of Vegetable— Materials. By H. C. REED. *Journal of the American Leather Chemists' Association*, Vol. 7, 1912, No. 6, pp. 307–334.

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Water; Determination of Free Carbon Dioxid in—. By H. NOLL. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 20, pp. 998–1005.

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Water Purification and the Prevention of Boiler Scale. By K. BRAUNGARD. *Chemiker Zeitung*, Vol. 36, 1912, No. 56, pp. 521–523.

Zinc; Production of— in the Blast Furnace with the Aid of Water Gas. By OSKAR NAGEL. *Chemiker Zeitung*, Vol. 36, 1912, No. 67, pp. 621–622.

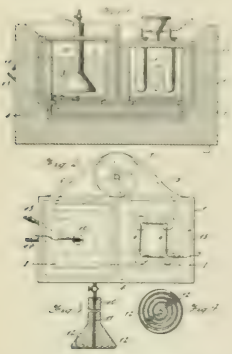
RECENT INVENTIONS

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

METHOD OF PRODUCING NITROGEN COMPOUNDS.

U. S. Patent No. 1,018,802, to Charles E. Acker, of Ossining, New York, Assignor to the Nitrogen Company of New York.

The patentee has discovered that a direct current of electricity from an alkali-metal alloy, e. g., sodium lead alloy, through molten alkali cyanid to a carbon cathode liberates the alkali metal in the pure state at the cathode; but if ammonia, hydrocarbon amins or their decomposition products, singly or mixed, or other suitable nitrogenous reagent be brought into contact with the surface of this cathode, while the current is passing, such reagent will instantly combine with the liberated alkali metal and carbon of the cathode, to form more alkali cyanid which immediately mixes with the mass of molten cyanid already present.

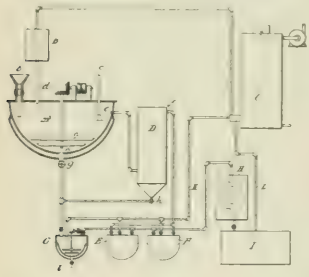


The hydrogen-carbon-nitrogen compound must have carbonaceous and nitrogenous constituents capable of combining to form a radical comprising carbon and nitrogen when the compound is reacted upon by the nascent metal.

METHOD OF MAKING ANHYDROUS TIN CHLORID.

U. S. Patent No. 1,018,805, to Gervais Baillio, of Niagara Falls, New York, Assignor to Castner Electrolytic Alkali Company.

A continuous process for converting metallic tin into anhydrous tin bichlorid on a commercial scale.



In manufacturing anhydrous tin bichlorid in the dry way, *i. e.*, by passing dry chlorin gas over metallic tin, sufficient heat is developed to melt the tin, and part of the tin forms stannic oxid, causing a loss of tin.

The patentee avoids any oxidation of the tin by submerging it in a quantity of anhydrous liquid, so that the tin is completely covered; chlorin gas is then applied. This operation must be carried out in a water-jacketed vessel fitted with steam connections, as temperature control is necessary. While the tin used may be perfectly pure, it is not necessarily so, as very satisfactory results have been obtained from a compound containing about 90 per cent. tin, the remaining 10 per cent. being composed of lead, iron and other impurities.

Carbon tetrachlorid or any suitable anhydrous liquid may be employed as the substance in which the tin is submerged, but the patentee recommends the use of anhydrous tin bichlorid for this purpose. When the chlorin is admitted to the tin bichlorid, or other anhydrous liquid, it attacks the tin contained therein and forms additional tin bichlorid. The latter is perfectly free from moisture (notwithstanding the fact that moist chlorin gas may be used) and may be drawn off from time to time, without interfering with the continuity of the process.

THE MANUFACTURE OF SODIUM CYANIDE.

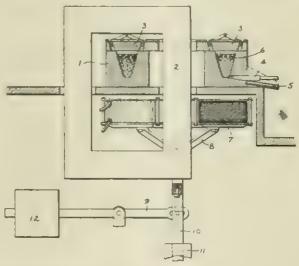
U. S. Patent No. 1,019,002, to Chas. E. Acker, of Ossining, New York.

This process consists in passing a current of electricity through an electrolyte of sodium and barium chlorides, using molten lead for the cathode; circulating the resulting alloy of sodium, barium and lead through the apparatus by means of a centrifugal pump; introducing a large amount of finely-divided charcoal in a reaction chamber, then lowering a plunger until slightly submerged; introducing at this stage fuel oil under pressure through this plunger and nitrogen through another pipe. The fuel oil is decomposed into hydrogen, which escapes, and carbon, which, with some of the carbon of the charcoal, forms barium carbide; the nitrogen combines with the barium carbide to form barium cyanide. The latter compound is then decomposed by the sodium, regenerating the barium and forming sodium cyanide which rises to the top of the bath, and can be drawn off.

INDUCTION FURNACE.

U. S. Patent No. 1,020,688, to Richard Fleming, of Lynn, Massachusetts, Assignor to General Electric Company.

This invention relates to electric furnaces of the induction type, in which the mass of metallic ore to be fused forms the closed secondary circuit of a transformer, the primary circuit consisting of a suitable coiled conductor in inductive relation to a magnetic core common to both circuits.



Heretofore it has been customary to incorporate the primary winding in the structure of the furnace, concentric with the core which passes also centrally through the circular crucible in which the ore to be smelted is placed.

As all parts are stationary, the apparatus calls for additional devices for regulating the current and adjusting it to the load; because with different quantities or qualities of ore, different quantities of current must be used.

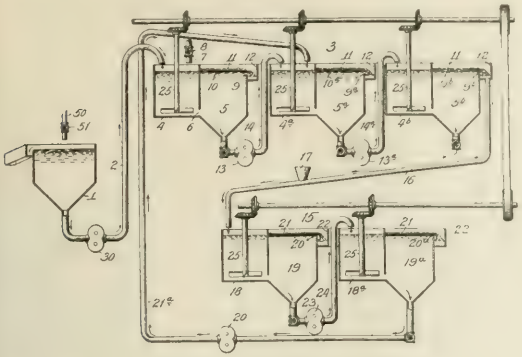
The object of this invention is to render the furnace self-regulating so that it will automatically adjust itself to any variation in load. This is accomplished by making the primary coil separate from the furnace as shown; and mounting it adjacent thereto in such a manner that it can move under the mutual repulsion which exists between it and the secondary circuit. A counterweight 12 tends to force the movable coil toward the crucible in order that the repulsion may be opposed until the current exceeds the desired strength.

ART OF CONCENTRATION OF MINERAL SUBSTANCES.

U. S. Patent No. 1,022,085, to James M. Hyde, of Basin, Mont.

This is a process of separating by flotation the valuable part of the mineral substance of ore pulps from the valueless or less valuable gangue minerals, by first preferentially coating the valuable part by means of a fat or oil whereby it exhibits markedly different surface tension phenomena from the remainder of the ore. The mixture is then agitated, permitting the valuable parts of the ore to float in the form of a froth which is separated from the balance of the ore by overflowing it together with

some water to insure overflow of the entire froth mass. The separated froth is subjected to a cleansing operation which consists in reagitating the concentrated material to free impurities entrapped therewith and permit the concentrates to



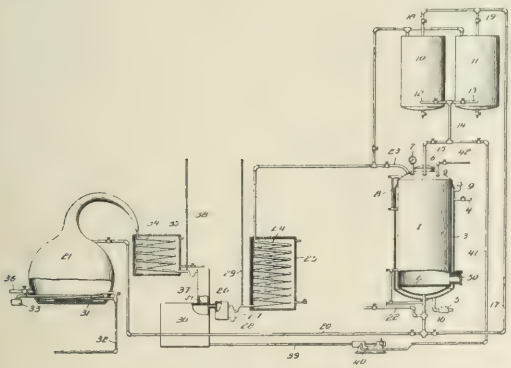
again form a froth. This froth is overflowed without any free flowing water and the settled impurities and the part of the froth not carried into the overflow is returned to the part of the pulp which is undergoing the separation treatment.

METHOD OF RECOVERING RESIN FROM WASTE PRODUCTS.

U. S. Patent No. 1,022,194, to Frank L. Huggins, of Wilmington, N. C., Assignor of one-half to John P. Moore, Jr., of Wilmington, N. C.

This process as carried out continuously is as follows:

The material is placed in the digestor 1 and a solvent, such as gasolene, is admitted from a solvent tank 11 to submerge the charge which is then heated. Steam is then admitted to the upper part of the digestor to expel the solvent through pipes 16 and 17 back to the tank 11. The residue in the digestor 1



is then removed and a fresh supply of material placed in the digestor and subjected to the action of the previously used solvent. This solvent is again forced back into the tank 11 and a supply of fresh solvent from tank 10 admitted. This after a heating operation is forced back into tank 10. Steam is then passed through the residue which is then ready for removal. The solvent is distilled from time to time in the still 21 to separate the resin.

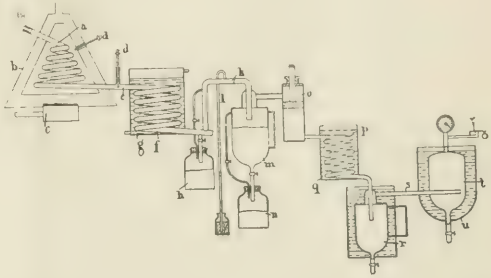
MANUFACTURE OF ISOPRENE.

U. S. Patent No. 1,022,338, to Oswald Silberrad, of Buckhurst Hill, England.

This is a process for the depolymerization of turpentine oil for the production of isoprene.

The invention consists in subjecting turpentine oil vapor to the action of heat having the pressure in the apparatus considerably below atmospheric pressure.

The apparatus, in which the process is carried out, consists of a heating coil, *a*, inside a heating chamber, *b*, heated by the products of combustion from a number of gas burners, *c*, using electric pyrometers, *d*, *d*, to determine the temperature. From



the heating coil, a pipe, *e*, leads to a water-cooling coil, *f*, situated in a water chamber. The hydrocarbons condensed in the coil *f* pass into a vessel, *h*, and the uncondensed vapors pass through a pipe, *k*, provided with a mercury gage, *l*, into another condensing chamber, *m*, from which further hydrocarbons are collected in the vessel *n*. The vacuum is produced by means of the vacuum and compressing pump *o*, and the vapors passing the pump pass through a cooling coil, *p*, immersed in brine. Isoprene is condensed in the coil *p*, and is collected in the chamber *r*. From the chamber *r*, the uncondensed vapor passes by the pipe *s* to the chamber *t*, immersed in brine. A blow-off valve, *v*, is provided from the top of this last condensing chamber.

PROCESS OF TREATING NATURAL GAS.

U. S. Patent No. 1,023,783, to Isaac N. Knapp, of Ardmore, Pa., Assignor to The United Gas Improvement Company of Philadelphia, Pa.

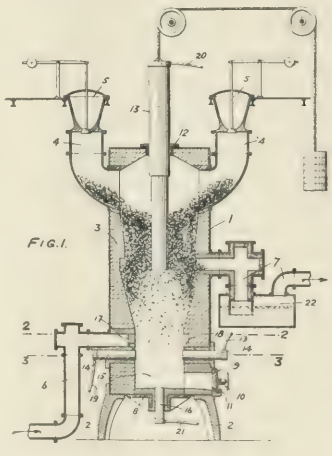


FIG. 1.

The purpose of the process is to make acetylene from natural gas. Natural gas containing approximately 92 per cent. to 97 per cent. of methane or marsh gas, CH_4, is passed through a bed of coke or coal from which air is excluded and which is maintained at a heat higher than that of ordinary or atmospheric combustion. The marsh gas is converted into acetylene, C_2H_2, the reaction being represented by the equation $CH_4 + 3C = 2C_2H_2$.

MARKET REPORT.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF JUNE.

ORGANIC CHEMICALS.

Acetanilid	Lb.	20½	@	23
Acetone (drums)	Lb.	17	@	18
Alcohol, grain (188 proof)	Gal.	2.55	@	2.57
Alcohol, wood (95 per cent.)	Gal.	50	@	52
Alcohol, denatured (180 proof)	Gal.	40	@	42
Amyl Acetate	Gal.	2.90	@	3.00
Acetic Acid (28 per cent.)	C.	2.00	@	2.15
Aniline Oil	Lb.	10¾	@	11½
Benzoic Acid	Lb.	23½	@	28
Carbon Tetrachloride (drums)	Lb.	nominal		
Carbon Bisulphide	Lb.	nominal		
Chloroform	Lb.	20	@	30
Carbolic Acid (drums)	Lb.	15	@	16
Citric Acid (domestic), crystals	Lb.	38½	@	39
Camphor (refined in bulk)	Lb.	44	@	—
Dextrine (imported potato)	Lb.	6	@	7
Dextrine (corn)	C.	3.05	@	3.26
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	19	@	21
Oxalic Acid	Lb.	8⅛	@	8½
Pyrogallic Acid (bulk)	Lb.	1.35	@	1.45
Salicylic Acid	Lb.	32	@	34
Starch (corn)	C.	2.28	@	2.58
Starch (potato)	Lb.	5¼	@	5¾
Tannic Acid (commercial)	Lb.	35	@	35½
Tartaric Acid, crystals	Lb.	30½	@	31

INORGANIC CHEMICALS.

Acetate of Lime (gray)	C.	2.50	@	2.60
Acetate of Lead (brown, broken)	Lb	7¾	@	8
Alum (lump)	C.	1.75	@	2.00
Ammonium Carbonate, domestic	Lb.	8¼	@	8½
Ammonium Chloride, gray	Lb.	6⅛	@	6¼
Aluminum Sulphate	C.	90	@	1.75
Aqua Ammonia (drums) 16°	Lb.	2¼	@	2½
Arsenic, white	Lb.	4½	@	5
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Barium Chloride	C.	1.40	@	1.55
Barium Nitrate	Lb.	4¾	@	5
Borax, crystals (bags)	Lb.	3½	@	4
Boric Acid, crystals (powd.)	Lb.	7	@	7½
Bromine, bulk	Lb.	25	@	30
Bleaching Powder (35 per cent.)	C.	1.25	@	2.00
Barytes (prime white, foreign)	Ton	18.50	@	22.50
Blue Vitriol	Lb.	5½	@	5¾
Calcium Chloride	C.	65	@	90
Chalk (light precipitated)	Lb.	4½	@	6
China Clay (imported)	Ton	11.50	@	18.00
Feldspar	Ton	7.00	@	9.00
Fuller's Earth, powdered	C.	80	@	85
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1.15	@	1.55
Iodine (resublimed)	Lb.	3.05	@	3.10
Lead Nitrate	Lb.	8⅜	@	8½
Lithium Carbonate	Lb.	65	@	70
Magnesite (raw)	Ton	7.50	@	8.50
Nitric Acid, 36°	Lb.	3⅞	@	4¼
Phosphorus	Lb.	35	@	90
Phosphoric Acid, sp. gr. 1.75	Lb.	22	@	26
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bromide	Lb.	31	@	34
Potassium Permanganate (bulk)	Lb.	9¼	@	9⅞
Potassium Cyanide (bulk) 98–99 per cent.	Lb.	19½	@	21
Potassium Iodide (bulk)	Lb.	2.45	@	2.50
Potassium Chlorate, crystals	Lb.	8¼	@	9½
Potassium Nitrate (crude)	Lb.	4¾	@	5
Potassium Bichromate, 50°	Lb.	6⅞	@	7
Quicksilver	Flask	40.50	@	42.00
Salt Cake (glass-makers')	C.	55	@	65
Silver Nitrate	Oz.	38¼	@	39
Soapstone in bags	Ton	10.00	@	12.00
Sodium Acetate	Lb.	4¼	@	5
Sodium Chlorate	Lb.	8¼	@	9½
Sodium Bicarbonate (English)	Lb.	2¾	@	3
Sodium Bichromate	Lb.	5	@	5¼
Sodium Hydroxide, 60 per cent.	C.	1.70	@	1.75
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent., spot	C.	—	@	2.45
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	6⅞	@	7⅝
Sulphur, Roll	C.	1.85	@	2.15
Sulphur, Flowers (sublimed)	C.	2.20	@	2.60
Sulphuric Acid, 60° B.	C.	85	@	1.00
Talc (American)	Ton	15.00	@	20.00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	13¼	@	13½
Tin Oxide	Lb.	46	@	50
Zinc Chloride (granulated)	Lb.	4¼	@	4½
Zinc Sulphate	Lb.	2¼	@	2½

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	40	@	44
Black Mineral Oil, 29 gravity	Gal.	12	@	12½
Castor Oil (No. 3)	Lb.	9½	@	10½
Ceresin (yellow)	Lb.	9	@	15
Corn Oil	C.	6¼	@	6.30
Cottonseed Oil (crude), f. o. b. mill	Gal.	43	@	47
Cylinder Oil (light, filtered)	Gal.	19½	@	20
Japan Wax	Lb.	9½	@	10
Lard Oil (prime winter)	Gal.	85	@	90
Linseed Oil (double-boiled)	Gal.	79	@	82
Paraffine Oil (high viscosity)	Gal.	25½	@	26
Paraffine (crude 120 & 122 m. p.)	Lb.	3	@	3⅜
Rosin Oil (first run)	Gal.	38	@	40
Spindle Oil, No. 1	Gal.	16	@	16½
Sperm Oil (bleached winter) 38°	Gal.	74	@	76
Stearic Acid (double-pressed)	Lb.	9	@	10
Tallow (acidless)	Gal.	62	@	65
Tar Oil (distilled)	Gal.	30	@	31

METALS.

Aluminum (No. 1 ingots)	Lb.	20	@	21
Antimony (Hallet's)	Lb.	7¾	@	8
Bismuth (New York)	Lb.	2.10	@	2.15
Copper (electrolytic)	Lb.	17⅝	@	17¾
Copper (lake)	Lb.	17¾	@	17⅞
Lead, N. Y	Lb.	—	@	4.40
Nickel	Lb.	50	@	55
Platinum (refined)	Oz.	46.35	@	47.00
Silver	Oz.	61⅜	@	61½
Tin	Lb.	48½	@	49
Zinc	Lb.	—	@	7

FERTILIZER MATERIALS.

Ammonium Sulphate	C.	3.35	@	3.40
Fish Scrap, domestic, dried	Unit	2.45	&	10
Blood, dried	Unit	2.72½	@	2.75
Tankage, high grade	Unit	2.60	&	10
Bone, 4½ & 50, ground, raw	Ton	27.00	@	—
Potassium, "muriate," basis 80 per cent.	Ton	38.55	@	—
Phosphate, acid, 16 per cent.	Ton	7.25	@	7.50
Phosphate rock; f. o. b. mine:				
Florida land pebble 68 per cent.	Ton	3.70	@	3.80
Tennessee, 68–72 per cent.	Ton	4.25	@	4.50
Pyrites, furnace size, imported	Unit	0.13¼	@	0.13½
Castor meal	Unit	nominal		
Mowrah meal	Ton	8.50	@	9.00

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume IV AUGUST, 1912 No. 8

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Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Penna., under the Act of March 3, 1879.

ESCHENBACH PRINTING COMPANY, EASTON, PENNA.

TABLE OF CONTENTS

EDITORIALS:
The Eighth International Congress of Applied Chemistry 556

ORIGINAL PAPERS:
The Manufacture of Carbon Bisulphide. By Edward R. Taylor 557
The Occurrence of Efflorescence on Lava Bricks. By William McGeorge 559
Enamels for Sheet Steel. By Robert D. Landrum 561
The Production of Excessive Hydrogen Sulfid in Sewage Disposal Plants and Consequent Disintegration of the Concrete. By William M. Barr and R. E. Buchanan 564
Marking Porcelain and Silica Crucibles, etc. By P. A. Yoder 567
On the Quantitative Estimation of Sodium Hydroxide in "Black Liquor." By Edwin Sutermeister and Harold R. Rafsky 568
The Chemistry of Anaesthetics, IV: Chloroform. By Charles Baskerville and W. A. Hamor 571
On the Starch of Glutinous Rice and its Hydrolysis by Diastase. By Yoshio Tanaka 578
The Effect of Sulfurous Acid on Fermentation Organisms. By W. V. Cruess 581
Concerning the Sugar Content of Watermelons. By Carl P. Sherwin and Clarence E. May 585
The Determination of Benzaldehyde in Maraschino Cherries and Maraschino Liqueur. By A. G. Woodman and Lewis Davis 588
Commercial Cinnamon and Cassia. By Harry E. Sindall 590
The Ripening of Hops. By C. E. Bradley and H. V. Tartar 591
Analysis of Some Fats of the American Buffalo (Bison). By Albert H. Schmidt 592
The Determination of Eucalyptol (Cineol) in Essential Oils. By Francis D. Dodge 592
Recent Analyses of the Saratoga Mineral Waters. By Leslie Russell Milford 593
Determination of Lithium. By Leslie Russell Milford 595
A New Volumetric Method for Tin. By Willbur W. Patrick and G. C. Wilsnack 597
A New Apparatus for the Volumetric Determination of Carbon Dioxide. By Howard W. Brubaker 599
A Modification of the Sweeney Method for Crude Fiber. By Cornelia Kennedy 600
Studies on Soil Humus. By Sherman Leavitt 601
An Examination of City Street Sweepings. By J. J. Skinner and J. H. Beattie 604
Inorganic Phosphorus in Plant Substances—A Method of Estimation. By R. C. Collison 606

LABORATORY AND PLANT:
Design and Equipment of the Chemical Engineering Laboratory at the University of Washington. By H. K. Benson 609
A New Apparatus for the Determination of Carbon Dioxide. By E. W. Gaither 611
Automatic Filter Feed. By Thos. A. Mitchell 613
Note on Protectors for Glass Stopcocks. By Walter O. Snelling 613
Alundum Crucibles in Gravimetric Analysis. By Guilford L. Spencer 614

ADDRESSES:
Natural Gas Investigations of the Bureau of Mines. By George A. Burrell 614
A Plan for the Support of Chemical Research and for the Better Teaching of Industrial Chemistry. By John Stewart 616

CURRENT INDUSTRIAL NEWS:
The Manufacture of Nitrates from the Atmosphere 619
A Process for the Fixation of Atmospheric Nitrogen 619
The Corrosion of Iron and Steel 619
Uses of Aluminum 620
Briquetting Metallic Waste 620
The Revival of the Kelp Industry 620
Lighting by Neon Tubes 620
"Granacit." 621
The Destructive Action of Acids on Concrete 621
"Ironizing," or "Ferrozincing." 621
A New Process for Electro-Zincing 621
Textilose 621
The Bleaching of Linen 621
Phosphorus Slag as an Insecticide 621
Oxygen Additions to Iron Furnace Blast 622
New Composite Sheet Metals 622
A New Use for Boron 622
Vanadium Babbitt Metal 622
A New Vacuum Gauge 622
A New Form of Valve for Gas-Cylinders 622
The Measurement of Steam Consumption 623
A New Joint for Steel Pipe 623

NOTES AND CORRESPONDENCE:
Sea-weed, Potash and Iodine. A Criticism 623
Nigerian Tin Developments 624
The Oil of Pochote 625
Lectures on the Smoke Problem 626
Detection of Formaldehyde in Foods 626
Laboratory Generator for Hydrochloric Acid Gas 626

BOOK REVIEWS:
An Introduction to the Study of Fuel; Annual Tables of Constants and Numerical Data, Chemical, Physical and Technological; The Chemistry of the Radio Elements; The Chemistry of the Rubber Industry; German Varnish Making; Industrial Organic Chemistry; Vinegars and Catsup, Interpretation of Standards, Analyses, Etc. 626

NEW PUBLICATIONS 628
RECENT INVENTIONS 629
MARKET REPORT 632

EDITORIALS

THE EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

Within a few weeks will occur an event of supreme importance to American Chemists and especially to those interested in the branches of our Science to which THIS JOURNAL is especially devoted:—the meeting, in Washington and New York, of the International Congress of Applied Chemistry. Strictly speaking, this is not the first time that such an organization has met on American soil, since the first impetus to the plan of these international meetings seems to have been derived from the sessions of foreign and American chemists who attended the Columbian Exhibition in Chicago in 1893. Every World's Fair has, in recent years, been accompanied by meetings of specialists in sciences and arts; but it must be remembered that they bear the relation of what is popularly called a side-show to the Exhibition itself. They are more or less haphazard in their relation to the general world of science and there is no continuity of management from one occasion to the next. The various international scientific congresses are autonomous; the experiences gathered at one meeting are utilized in the preparation for the next one; special problems are committed to the care of qualified experts, for the report of authoritative opinion to the next gathering and the way is paved for that general world-wide coöperation in the advancement of knowledge and the perfection of its utilization, which has been within narrower limits the chief virtue of the various national organizations.

It is just 250 years since the Royal Society was incorporated in London,—with the sole exception of the Accademia du Lincei—probably the oldest extant society for the exchange of knowledge between the devotees of exact and natural sciences. For nearly two centuries these societies were not only close corporations but also practically local clubs. The greater diffusion of scientific learning, as well as the increased means of communication by railroad and telephone, led to the establishment of national associations, with more liberal terms of membership, and various associations for the advancement of science, with the added feature that the meetings were never held twice in succession in the same city. A natural outgrowth were the national societies for the promotion of some particular science; since increased specialization made it possible for anybody to follow understandingly the sessions of a general association, which soon met in sections, that naturally led to a demand for a closer form of union of their respective members. So that, in chemistry at least, each great nation now possesses one or more special societies, not restricted as to localities or qualifications, as is the case with the academy or institute, but open to every person interested in the science. At the last annual meeting of the American Chemical Society, there were assembled as many members as would have been deemed a fair attendance for the entire American Association for the Advancement of Science, not so many years ago. It is not necessary to descant here on the advantages of oral discussion, supplemented by the pleasures of social intercourse, which make these general sessions so attractive, any more than it is important to point out the same gregarious instinct, which has led to the successful institution of so many local sections, with their well-attended stated meetings. But we must emphasize the fact that *local* chemical societies led a very precarious existence until the more powerful national organization enabled them to gather strength by coöperation and let them experience the stimulus of generous rivalry.

And now we have entered into a new era, practically with the opening of the XXth Century, that of the utter abolition of national boundaries so far as scientific endeavor is concerned. A new chemical discovery in Paris is known in London, New York and Tokio in far less time than was consumed in the transmission of Priestley's or Cavendish's communications to the Royal Society in London, and the time is rapidly passing when the possession and guarding of a scientific secret could be deemed a national advantage. If it be deemed conducive to international amity that the young men of all nations should meet at the Olympian games, in contests of brawn and motor-nerves, how much more important is it that there be occasional interchanges of thought and knowledge. And yet, we wonder whether the press of New York will afford as many paragraphs to the forthcoming International Congress of Applied Chemistry, for matter supplied to it free of expense, as it has published pages of expensive cablegrams from Stockholm? We do not expect any mobs of frenzied cheerers to throng around the arena of scientific debate; and yet we know that the impression which our foreign visitors will take home of the progress in American science and scientific industry will be of far greater importance to the esteem in which our country will be held abroad, than the number of cups which the Finland will bring home from Stockholm. Our individual responsibility in this Congress is as great as our individual opportunity.

To meet the leaders of chemical knowledge and of chemical manufacture, from abroad as well as home, to listen to a free exchange of thought and practical experience, are privileges for which innumerable chemists have traveled to Berlin, London, Paris, Vienna and Rome. We all now have these chances at home, coupled with the opportunity to benefit by free and generous criticism of whatever we may desire brought to their view. In chemical industry, at least, medieval secretiveness is breaking down in favor of frank exchange of experiences.

That the scientific importance of the approaching Congress is thoroughly realized may be gathered from the fact that upwards of 600 papers have already been accepted and are being printed, ready for distribution at the Congress itself. In view of the stringent rules

of acceptance which have been adopted, and the early date set for the submission of the papers themselves, it would probably have been easier for the authors to secure publication in the journals of their respective national chemical societies, had they not recognized the paramount claims of this International scientific gathering.

The American Committee of Arrangements is bending every effort toward making the sessions agreeable to the participants; they are particularly anxious to make this Congress memorable for the promptness with which it shall transact its business, the smoothness with which the machinery of entertaining its members shall revolve and the completeness with which their comfort may be considered. This means as full coöperation on the part of every American chemist as has been cheerfully afforded by the hard-working members of the various committees. It may be taken for granted that every chemist who can get away from his work, no matter in what part of the United States he resides, will be anxious to attend the Congress, not only for the selfish reasons already stated, but also for the patriotic one of adding by his own presence to the prestige of the greatest chemical function which is likely to occur here for many a year.

But it is not fair to the managers that you should leave them in the dark as to your intentions: mere subscription to the Congress does not necessarily mean attendance. Write to the Reception Committee at the Chemists' Club, 52 East 41st Street, New York City, of your purpose to come on; of your probable address; of the ladies who will accompany you. If you desire it, write also the kind of rooms you wish to have reserved for you, with your preference of hotels, as this committee has undertaken to look after all the personal comforts of the members. If you have not even paid your subscription as yet, do not postpone this duty until your arrival here, but attend to it now! Remember that no hostess feels happy if she is in doubt as to the acceptance of a single guest, and that there are all kinds of functions planned for this Congress, which cannot be completely arranged, until the approximate number of participants is ascertained. The man who waits until the last minute unless compelled to do so, "because there is always room for one more," catalyzes more profanity among his colleagues than his conscience can bear. Do your share, in the matter of *time* as well as personal attendance. You will not be sorry.

ORIGINAL PAPERS

THE MANUFACTURE OF CARBON BISULPHIDE.[1]

By Edward R. Taylor.

Received May 22, 1912.

The radical changes that have been made possible by the use of electricity in chemical industries are well exemplified in the advance in the manufacture of carbon bisulphide during the past thirty-five years. Reports have been made on the progress of this work from time to time.[2]

The old retort method of manufacturing bisulphide of carbon was fraught with many annoyances and disagreeable circumstances. Yet at one time I had as many as twelve of them in running condition. With but one retort in a place, economies vanish rapidly. With a number in the same furnace they are not all likely to fail at the same time, but one is constantly taking out and putting in, which keeps the works in a state of confusion all the time. Fortunately, the large dynamo, with its ability to generate electricity in large quantities and at reasonable rates, has come to our aid. In any of the usual retorts we are limited as to sizes of retort by possible heat penetration to the interior. As these old retorts are heated externally, you will appreciate some of the difficulties of their operation.

With the electric retort, however, we can have the heat in the interior, where we want it and keep the shell cool; that is the secret of its great success.

In regard to the development of our electric retort, I had considered numerous ways of conducting electricity into the furnace, and gave up as inadvisable the idea of using movable electrodes as is ordinarily done in furnaces. I concluded if I could substitute for that some electrical conductor in small pieces which would come in between stationary electrodes and stand the brunt of the stress, I would overcome the necessity of moving the electrodes, and this has been so successful that we have been able to run our furnace anywhere from eight months to a year without shutting down, and we have made from 1,500,000 to 2,000,000 pounds of carbon bisulphide in a furnace without cleaning out.

Two large induction type dynamos, made by the Stanley Company, are used in producing the electricity to supply our furnace and have given excellent satisfaction. A waterfall and lake furnish regular water-head for the turbine generator. A Corliss engine helps out the water power. Two cables convey the elec-

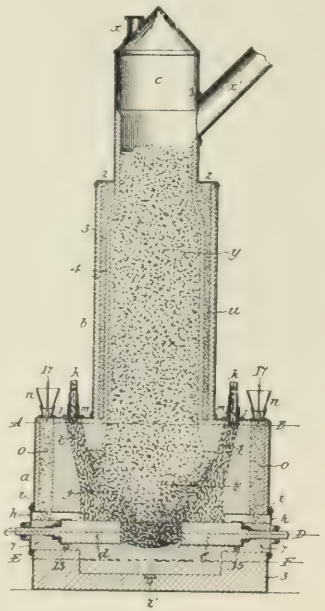

Fig. 1.

[1] Presented before the New York Section of the American Chemical Society, May 10, 1912.

[2] *Trans. Am. Electrochem. Soc.*, **1**, No. 1, 115-7 (1912). *J. Frank. Inst.*, Feb., 1908.

tricity from the dynamos to aluminum bars 6" wide and 5/8" thick, which are connected with the insulated electrodes. Aluminum is used in preference to copper because it is less liable to corrosion. Careful and absolute insulation from the shell of the furnace is necessary and possible

Figs. I and II show the interior construction of the furnace. Each composite electrode in this furnace is composed of twenty-five carbons each 4" × 4" × 48," making a complete electrode twenty inches square and forty-eight inches long. We use two-phase alternating current and four of these electrodes. In the center of the furnace they are about twelve inches apart.

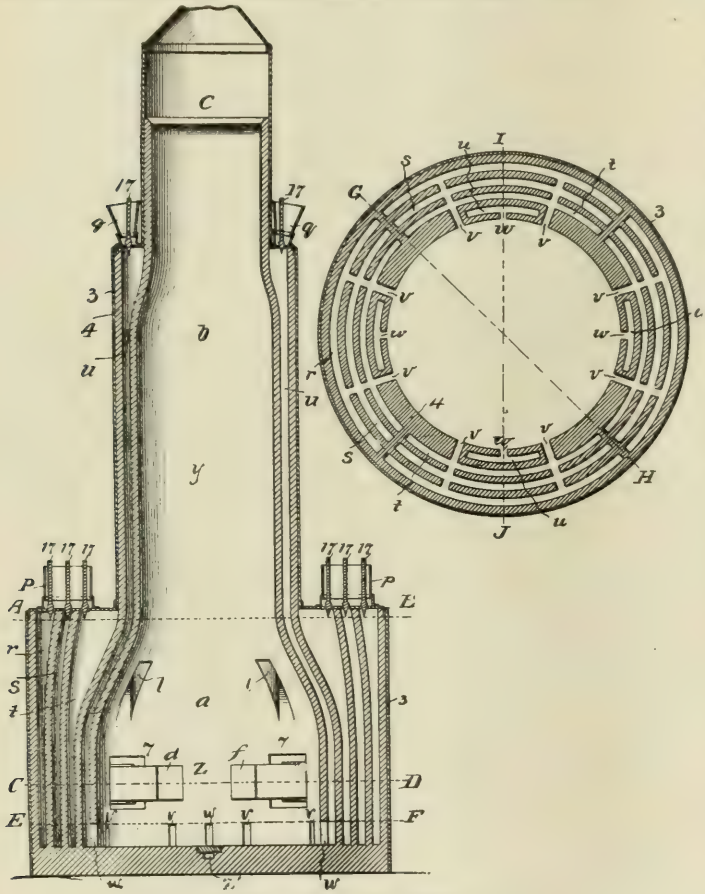

FIG II. HEIGHT, 41 FT. DIAMETER, 16 FT.

Chimneys above each of these electrodes are used to convey broken carbons down upon them and over their ends. Their action breaks up and diffuses the current which, instead of being of one or two arcs, is broken up into a multitude of little ones, but these probably disappear as the furnace heats up. This moderates the intensity of the heat, stops entirely the hissing of the current so common in arc furnaces, and protects from excessive wear the main and more expensive electrodes, which last a year or more without renewal.

They also, if possible, serve a still more important purpose in regulating the current and saving the necessity of moving the electrodes through the walls of the furnace, which would be a very troublesome thing to do in a furnace filled with melted and vaporizing sulphur. This was a problem that presented very serious features in the early thought of a furnace for this purpose. The broken carbons also relieve the intense violence of the heat at the terminals. It will be appreciated that for low temperature work, like the manufacture of bisulphide of carbon, this is very essential. They also facilitate the starting and stopping of the furnace. Indeed the broken carbons are so valuable in this respect that we find we can stop and start at will, even when the furnace has become completely cold, and I cannot emphasize too highly the value of these broken carbons in a furnace of this construction.

To charge the furnace, sulphur is filled in up to the top of the electrodes and broken carbons are added, including the filling of the different chimneys over the several electrodes; the shaft of the furnace is filled with charcoal, and the periphery spaces of the furnace filled up with sulphur.

With the large construction, it is easy to feed the cold and crushed sulphur around the periphery of the furnace, allowing it to find its way in the melted state into the interior heat zone.

Being progressively raised in temperature as it approaches the zone of reaction, the level of the melted sulphur is regulated by the amount of current supplied to the furnace and the amount of cold sulphur fed into the periphery.

On combination of the sulphur vapor with the charcoal, the formed bisulphide of carbon rises through the charcoal above it, heating it as it progresses downward towards the reaction zone.

Thus, in this furnace, the heat seeking to escape by radiation is continuously borne back to the reaction zone by the incoming material.

So complete is this return that, when making bisulphide of carbon at the rate of fourteen thousand pounds per twenty-four hours with the room at 16° C., the outside shell of the furnace shows temperatures at different points ranging from 23–64° as a maximum: with yet more power in the furnace, the production would be greater and these readings still lower.

There is very little wear to the interior of the furnace. If electrodes are disposed to get very hot, we feed a little more sulphur than otherwise, and that has a tendency to cool the electrodes.

Sometimes pillars are disposed to form in the cor-

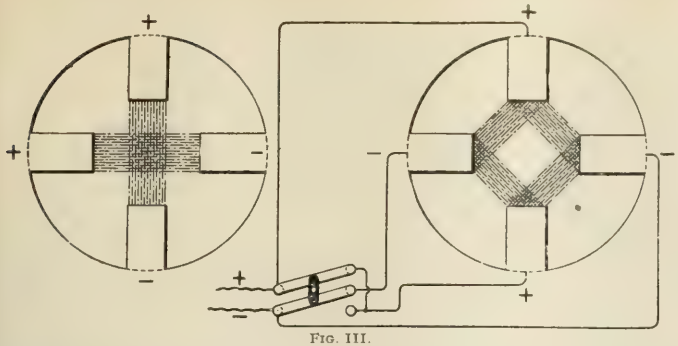

FIG. III.

ners between the electrodes. We use the 2-phase current, with one phase put on one side and the other phase on the other. Now, if pillars form in the corners, and the conductivity of the furnace is not just right, we sometimes change over and run the current to adjacent electrodes to burn out the pillars. This change is shown in Fig. III.

The provision for the sulphur is, I believe, one of the most important features of the furnace structure. We are able to lag the furnace from the inside instead of outside, and we lag it with the very materials used in the production of the carbon bisulphide.

Now the more perfectly we can carry this out, and the more completely full all of these channels can be kept with sulphur, the greater the economy will be in the production of the goods. The real fact is I have never yet been able to put enough current into one of these furnaces to enable us to keep all of these perfectly full. I am looking forward in a few weeks to being able to do that, and I anticipate that I shall be able to produce from 25,000–30,000 lbs. of carbon bisulphide in one of these furnaces in twenty-four hours. We have already produced 16,000 lbs. in twenty-four hours, as it is, but with sufficient power to go into the same furnace, it will practically double the output.

PENN YAN, NEW YORK.

CARBON BISULPHIDE PLANT, PENN YAN, NEW YORK.

THE OCCURRENCE OF EFFLORESCENCE ON LAVA BRICKS.

By WILLIAM MCGEORGE.

Received March 20, 1912.

It is a common occurrence to see brick walls partially covered with a white film generally most abundant under the eaves and window-sills but more or less scattered over the whole building. This film is composed of soluble salts which, being washed from the interior, on appearance at the surface and subsequent evaporation of the water are deposited as a film. In most cases it is composed of sulphates of calcium, magnesium, potassium or sodium. The carbonates of calcium and magnesium are considered too insoluble to appear and those of sodium and potassium too

soluble to remain on the surface of the brick. This film may be attributed to several causes, a few of which are as follows: (1) presence of soluble salts in the materials used, (2) soluble salts formed directly or indirectly through the action of the vapors in the drying kiln, (3) soluble salts formed through the action of the mortar after the bricks have been placed in the wall.

Undoubtedly most of the cases of efflorescence may be traced to cause (1); namely, the presence of soluble matter in the material used. In our case it was noticed that the appearance varied with the degree of porosity or compactness of the finished brick, the more porous brick being covered with a heavy film soon after being placed in the yard. The more compact ones being less easily penetrated by the rains kept their natural appearance longer or did not have so heavy a film.

The Honolulu Lava Brick Company is making brick from dark gray basaltic lava rock such as is used for building purposes in the islands. This rock exists in large quantities on this island (Oahu) and contains a comparatively high percentage of water soluble matter. Their process is essentially as follows: the rock is ground in a mill to a fine powder, to which after the addition of a small per cent. of lime, cement or both, according to formula, enough water is added to dampen the mixture. The whole is then run into a press and pressed into brick. They are then dried in a manner best suited for the setting of the lime or cement. The resulting product has shown excellent physical tests and is a good grade of building brick of gray color. It has been noticed, however, from the beginning, that some of the bricks, soon after being wetted by the rain, became covered with a heavy white efflorescence. At first it makes its appearance in the form of needle-like crystals shooting out from the pores of the brick. Later as the quantity increases the deposit becomes heavy and can be scraped from the surface in large amounts.

Without ascertaining the composition of this film the company tried several methods of eradicating it, which had been recommended by different people. Two of these were addition of barytes which had little or no effect, and the painting of the surface with oil, which in this case did not even have a temporary retaining effect.

Upon making an analysis of this film it was found to be composed essentially of a mixture of sodium and potassium carbonates. The following is a complete analysis:

SiO_2	0.85	H_2O	24.32
Fe_2O_3	..	Na_2O	29.81
Al_2O_3	0.93	K_2O	10.14
P_2O_5	..	SO_3	0.32
CaO	1.56	Cl	0.20
MgO	0.42	CO_2	31.39

It may be seen at a glance that it is composed of extremely soluble constituents. In fact, it may be dissolved by placing in the palm of the hand and rubbing with the finger. On the other hand it does not agree very closely with the composition of the soluble matter existing in the rock.

Composition of Lava and Lava Disintegration Products[1]

	I.	II.
SiO_2	52.15	23.28
Al_2O_3	12.57	33.77
Fe_2O_3	3.36	13.31
FeO	7.07	3.08
Mn_3O_4	0.50	0.40
CaO	8.54	0.16
MgO	6.51	0.09
K_2O	0.84	0.23
Na_2O	2.64	0.29
P_2O_5	0.28	0.32
SO_3	0.61	0.46
TiO_2	4.07	4.49
Vol. matter	0.57	14.53
H_2O	0.37	6.90

[1] From analysis by W. P. Kelley.

The above table shows the effects of weathering and disintegration upon lava rock and incidentally the soluble and insoluble constituents. Column I is an analysis of lava rock and II is its disintegration product taken out of the gulch at the edge of I where the rock was badly disintegrated and most of the soluble matter washed out into the soil. The samples were taken very close to each other and were originally of the same composition. Hence these analyses show conclusively that the major part of the soluble matter is calcium, magnesium and silica, while sodium and potassium are of only secondary importance. It may be stated at this point that the lava rock mass contains little or no carbonate, but a large percentage of these lavas have a vesicular structure and these vesicles or holes are in many cases coated with a film of salts, varying in composition. Some of these are composed of carbonates. While the above table shows the relative solubility of the various ingredients it presents no data which would hinder one from concluding that the sodium and potassium were dissolved out more quickly during the weathering stages than the other ingredients, even though a larger relative percentage of them remains in the residue. If this were true it would account for the small percentage of calcium and magnesium in the film. Accordingly, a set of leaching experiments were run to ascertain if the above were true and to test out the possibility of leaching the ground rock before pressing, thereby removing the soluble matter as far as possible from the material. The results of leaching the ground rock are shown in the following tables, and proved entirely impracticable. Although the soluble matter of which the film is composed decreases, it does so only to a slight extent, while the calcium and magnesium are leached out very rapidly as sulphates.

Solubility of Crushed Lava in Hot H_2O.

	I.	II.	III.	IV.
SiO_2	0.97	17.30	16.05	16.17
CaO	13.75	0.26	0.28	0.27
SO_3	36.48	5.04	3.50	2.28
MgO	3.98	0.18	0.56	0.21
Na_2O	32.10	21.66	34.78	16.10
K_2O	1.86	1.54	5.46	4.65
Res. in 100 cc.	0.9851	0.9516	0.8288	0.7442

The above table shows the results obtained by leaching the ground rock with hot water for eleven

days. Leachings were made by allowing the ground rock to remain in an iron tank containing hot water. After one hour the leachings were drawn off and the partial analysis made on this solution is shown in column I. Fresh hot water was then added and allowed to remain twenty four hours and this repeated for eleven days. Column II represents the partial analysis of the solution obtained after one day in contact with the ground rock following the one-hour extraction, column III, that on the fourth day and IV, the eleventh day. Constituents are given in percentages in solids obtained from leaching waters and grams of solids per 100 cc. of solution are shown at the bottom. The first leaching was neutral to litmus and all the rest were decidedly alkaline.

Leaching with cold water was also tried but the experiment was stopped at the end of the third day. A glance at the following table will show that the action of the hot and the cold water was about the same except that the latter was much slower.

SOLUBILITY OF CRUSHED LAVA IN COLD WATER.

	1 hr.	2 days.	3 days.
SiO_2	1.44	13.28	15.30
CaO	20.92	6.53	5.16
SO_3	28.26	11.08	10.68
MgO	0.94	6.32	6.04
Na_2O	14.58	21.76	45.52
K_2O	1.78	5.56	6.06
Res. in 100 cc	0.4637	0.0594	0.0638

This table also shows percentages in the solid matter in the leaching waters and grams of solid matter in 100 cc. Bricks made from the leached rock also developed efflorescence. The major part of the difference between the sum of the constituents recorded in both of the above tables and 100 per cent. is made up of CO_2 and water of crystallization. In the analyses of the extracts, the water and carbon dioxide varied greatly and were not considered to be of sufficient value to warrant their determination.

In addition to these leaching experiments a number of finished bricks were submerged in water to ascertain if a sort of osmosis could be set up within the brick by which a large percentage of the saline matter would be retained in the interior of the brick. They were submerged for various periods and it was found that it gave only temporary benefit.

Barium carbonate and chloride have been used as a means of removing soluble sodium and potassium compounds, their action being to replace the alkalis and form harmless by-products, the alkali compounds being washed out. However, this method has been used only in the wet process and in cases where the percentage of sodium is much less than ours. As stated above when used in our case it had no effect and altered very little the indefiniteness of the time it would take the various weathering agents to remove the salts by the washing of the rain, evaporation and drawing to the surface of more saline matter.

Upon further investigation it was noticed that those bricks to which lime had been added invariably gave a thick efflorescence, increasing with an increase in the percentage of lime added. Then this same rock has been used as a building stone in its natural state and while it is quite porous has rarely shown any of the above efflorescence when used as such. From these facts it appears that the addition of lime is the cause, at least in part, of the trouble. On the other hand it is absolutely necessary to add some binding material to hold the brick together after it comes from the press. While a brick may be made simply by dampening the ground rock and pressing, the corners chip easily upon handling.

Since there seemed to be no chemical means of complete removal or precipitation of the saline matter and addition of lime was partly the cause of the appearance of the film, through its alkaline action on the sodium and potassium and subsequent conversion of these into carbonates, the problem narrowed down to an elimination of the lime, if possible, and the addition of a binding agent which would give a more compact brick as well as one which might have some osmotic properties.

Potassium and sodium are known to occur in basaltic lava in the form of complex silicates. From this fact it is apparent that these silicates are acted upon by the lime, since the bricks after being pressed are run into drying kilns and heated under pressure with steam. The lime, under pressure and at the high temperature of the kiln, reacts with the sodium and potassium in the complex silicates and forms caustic soda and potash as by-products which upon appearance at the surface are converted by the carbon dioxide of the air into carbonates and bicarbonates of the alkalis. If this were true then an elimination of the use of lime as a binding agent should eliminate the trouble. This was done and a small per cent. of cement was used in its stead and the method of drying altered. In this way a more compact brick was obtained and at present writing the alteration is producing decidedly better results.

Thanks are due Mr. W. P. Kelley for valuable suggestions; also for the analyses showing effects of disintegration on lava rock, these analyses being taken from investigations made by him on lava disintegration.

CONTRIBUTION NO. 4, FEDERAL EXPERIMENT STATION,
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ENAMELS FOR SHEET STEEL.[1]

BY ROBERT D. LANDRUM.

Received April 4, 1912.

Enamels for sheet steel are boro-silicates of sodium, potassium, calcium and aluminum and are, in every sense of the word, glasses. Such enamels are so compounded that they form a homogeneous, glossy coating on the surface of the sheet steel utensil, which will not be corroded by the acids or alkalies used in cooking and which will resist punishment both by impact and by rapid changes of temperature.

Although an enamel is a glass, the fact that it must adhere to steel and resist the abuse common to cooking utensils makes necessary the addition of other ingredients besides those used in manufacturing ordinary glass. In enamels, ground quartz, flint or sand supply the silica, and feldspar and clay, the alumina. Fluor-

[1] Delivered before the Chemists' Club of Rochester at the University of Rochester, Rochester, New York, April 1, 1912.

spar or calcite is added to supply the lime and cryolite to render the enamel translucent. Soda ash and pearl ash are fluxes adding sodium oxide or potassium oxide to the product, and borax furnishes the boric anhydride, which adds many desirable qualities, such as greater ductility and elasticity. Sodium or potassium nitrate is used in white enamels and manganese dioxide in dark colored enamels as an oxidizing agent. Oxide of cobalt is used in enamels which come directly in contact with the steel and adds adhesiveness to this coating.

For producing white enamels, oxide of tin is used; for blue, cobalt; for violet and brown, manganese; for gray, nickel; for green, copper or chromium; for yellow, uranium or titanium; and for red, iron, selenium or gold.

Enameling is still held as a secret art, and the formulas are carefully guarded. Most companies allow very few visitors to go through their plants and some keep their employees in ignorance by various schemes. In one American works, each of the enamel raw-materials is given a number. They are ordered, shipped, kept account of, and stored under their respective numbers, and only those in authority even know what materials are used. In this same factory, employees of one department are not allowed in another and after being employed in one department, a man is barred from employment in any other. Some works have the formula for each enamel divided into two parts, one of which is mixed by one man, the other by a second, and certain proportions of each are then mixed together by a third man. In practically all enameling works, the materials are weighed on a scale, the beam of which is hidden from the laborers, who are also generally of foreign birth and are changed frequently.

The "Black Shape."—The sheet steel which is used for enameled ware is as nearly as is possible free from carbon, silicon, sulphur and phosphorus, and its manganese content is generally about 0.2 per cent. These sheets come in squares and oblongs from 27 to 20 gauge and are circled, stamped and spun with as little heat treatment as possible and with the use of a lubricant that can easily be cleaned off. The ears, handles and other trimmings are, as far as is practical, welded on, as riveted joints are difficult to enamel.

Pickling Process.—The surfaces of the completed steel vessels are thoroughly freed from carbonaceous matter by annealing at a low red-heat and are then pickled in hot dilute acid, thoroughly rinsed in water, and then in weak alkali solution. After a quick drying they are ready to be enameled.

The Enamel.—In the making of an enamel, the various raw-materials are loaded from their respective bins into small cars called "dollies." These are filled to a line which approximates the correct weight, then they are pulled on a scale, the beam of which is hidden from the workman, and the enamel-master indicates whether the load is light or heavy, and the workmen correct this by shoveling on more or taking some off. When each of the "dollies" is corrected so that the required amount of material for a mix is in it, all are dumped on a large, hard maple floor, the coarser material on the bottom and the finer on the top. This pile is thoroughly mixed by shoveling, and is loaded into an electric elevator, which hoists it to its bin. There is a bin for each different kind of enamel, and a traveling bucket which holds a melt (about 1200 pounds) carries the mix to the tank furnaces where it is melted into a liquid glass.

These tank furnaces are regenerative, reverberatory furnaces like those used in the manufacture of glass, and natural gas or crude oil is an ideal fuel for them. However, in the older enameling works, coal is used directly, and in the later ones producer-gas is used as a fuel. The temperature required for smelting the different enamels varies from 1000° C. for a glaze to 1300° C. for a ground coat, and, in most enameling works, pyrometers are installed to assist in controlling these temperatures. Each furnace will give seven or eight melts in twenty-four hours.

After the enamel is melted into a liquid glass, a fire-clay plug in the front of the furnace is pulled out and the glowing liquid stream plunges out and is caught in a tank of cold running water. The reaction is terrific and the glass mass is torn and shredded, cracking into small pieces like popcorn, each of which is a myriad of microscopic seams and fissures. This "quenching," as the process is called, toughens the enamel and facilitates the process of grinding which comes next.

The water is drained from the tanks, leaving the "enamel frit." This is shoveled into pans (a certain weight to a pan) and is ready for grinding.

In the mill room, the enamel frit is ground in large ball mills for about thirty hours. These mills are cylindrical, about five feet long and six feet in diameter, and are lined with porcelain bricks. The frit is put into them with fifty per cent. of water and several per cent. of white ball-clay. For the white cover-coat enamels, tin oxide is also added. The mill revolves and the constant impact of the flint stones against the glass particles grinds them to an impalpable powder, which mixes with the water and the clay, forming a mass which has the consistency of rich cream. This is loaded into tanks, where it is allowed to age a week or so.

Application of the Enamel.—From the mill room the enamel is taken to the dipping room, where it is put into tanks that are like large dish-pans. These are sunk into tables, and at each tank a slusher works. The slusher takes the stamped-out steel vessel, which has been thoroughly cleaned, and plunges it into the enamel. When taken out, the wet enamel forms a thin film over the entire surface. By a gentle swinging motion, the excess of enamel is thrown off, and the vessel is placed bottom down on three metal points projecting from a board. Three or four vessels are put on a board; these are placed on racks and when the vessels are thoroughly dry they are carried to the furnace room.

The furnace room contains a long bank of muffle-furnaces and in these the ware is put after drying. The temperature in these furnaces is about 1000° C. and here the little powdered particles of enamel are

fused together in a solid glass coating over the vessel, the process requiring from three to five minutes.

Each coat is burned separately. For instance, we have a pudding pan that is to be a three-coat white inside, turquoise-blue mottle outside. It is first dipped in the ground coat enamel, the excess is shaken off and the vessel put on a three-pointed rack and dried. After drying, the enamel stands in little grains all over the surface of the ware, adhering to the metal on account of the raw clay ground with it. At this stage every care must be taken, for a scraping, even of the finger nail, would take off some of the powdered particles of the enamel. This pan is then put into the muffle of the furnace, and the heat fuses all the little particles together, leaving a tight-holding vitreous coating all over the surface of the vessel. This fundamental coating is nearly black, due to the oxides of cobalt and nickel which it contains, and shines with a glass-like luster.

After the vessel has cooled at the ordinary temperature of the room, it is again brought to the slushing room, and here is covered with an enamel—this time a white. It goes through the same process as before, except that a black bead is brushed around the rim. On account of the dark color of the first coat showing through, this second coat, after it is burned, has a gray appearance, and is called the "gray coat" or "first white." The vessel is again sent to the slushing room, and is dipped into a white enamel, the excess shaken off, and before drying the blue-green enamel is sprayed on the outside.

This spraying process was at one time done by dipping a wire brush into the wet blue-green enamel and the slusher shaking it over the surface of the vessel, causing the blue enamel to fall in little speckles all over the white enamel. In most factories, however, spraying machines, which work on the principle of an atomizer, have been installed. A tank full of the colored enamel stands over the table and the enamel is forced out through a nozzle in a spray by compressed air. The flowing of the enamel is controlled by the foot of the slusher as he holds the vessel in the spray. The vessel is then dried and the coating is fused in the muffle-furnace, the result being turquoise-blue spots on a white background.

The finished ware is assorted into three lots: firsts, seconds, and job lots. Some of the seconds and job lots are fit for redipping. They may have some little spots where the original vessel was not properly cleaned and where, on account of the rust or dirt, the enamel did not adhere. These spots are filed or are held under a sand-blast until the exposed surface is perfectly clean, and then the vessel is covered with another coat of enamel.

There are schemes for saving money in all manufacturing plants, and in the enameling business a large part of the profit comes from the residues. For instance, every bit of enamel is scraped from the tanks and tables, all sweepings from floors are saved, and all the waste water from the various departments is first carried into catch basins, and every few days these are cleaned and the residue, which has settled to the bottom, is taken out. The residues from all these sources are again melted with the proper amount of fluxing material and coloring matter, and this dark-colored enamel is used for coating the cheaper wares.

A German White Enamel.—In order to give an idea of the composition of a white cover-coat frit, such as is used on cooking utensils, and to show the method used by ceramists to calculate its so-called molecular formula, the following enamel, the formula of which is taken from the 1911[1] edition of the "Taschenbuch für Keramiker," is used:

Feldspar 38.6 per cent., quartz 19.0 per cent., borax 15.4 per cent., cryolite 11.7 per cent., saltpeter 6.5 per cent., calcite 6.5 per cent., fluorspar 1.3 per cent. and magnesium carbonate 1.0 per cent.

Enamel Materials.—All the materials used were practically pure except the feldspar, which was a pegmatite of the following composition:

		Per cent.
Silica	(SiO_2)	70.66
Alumina	Al_2O_3	16.85
Potassium oxide	K_2O	5.93
Sodium oxide	Na_2O	4.61
Lime	CaO	0.52
Carbon dioxide	CO_2	0.41
Moisture	H_2O	1.02

This figures to a "molecular" formula of

$$\left.\begin{matrix}0.45\ Na_2O\\0.39\ K_2O\\0.06\ CaO\end{matrix}\right\}\ Al_2O_3\left\{\begin{matrix}7.11\ SiO_2\\0.34\ H_2O\\0.06\ CO_2\end{matrix}\right.$$

the molecular weight of which would be 602.

The other materials used were:

Material.	Formula.	Equivalent weight.
Quartz	SiO_2	60
Borax	$Na_2O{\cdot}2B_2O_3{\cdot}10H_2O$	382
Cryolite	$2Na_3AlF_6$, giving $3Na_2O{\cdot}Al_2O_3{\cdot}6F_2$	420
Saltpeter	$2K_2O{\cdot}N_2O_5$	202
Calcite	$CaO{\cdot}CO_2$	100
Fluorspar	CaF_2, giving $CaO{\cdot}F_2$	78
Magnesium carbonate	$MgO{\cdot}CO_2$	84
Feldspar	(Given above)	602

THE ENAMEL.[2]

Batch Mix. Material.	Per cent. used.	M. W.	Molecular equivalent.[3]	Na_2O.	K_2O.	CaO.	MgO.	Al_2O_3.	SiO_2.	B_2O_3.	F_2.
Feldspar	38.6	602	0.0641	0.0288	0.0250	0.0038	..	0.0641	0.4558	..	..
Quartz	19.0	60	0.3167	..	..	..	..	..	0.3167	..	..
Borax	15.4	382	0.0403	0.0403	..	..	..	..	..	0.0806	..
Cryolite	11.7	420	0.0279	0.0837	..	..	..	0.0279	..	..	0.1674
Saltpeter	6.5	202	0.0322	..	0.0322	..	..	..	..	..	..
Calcite	6.5	100	0.0650	..	..	0.0650	..	..	..	..	..
Fluorspar	1.3	78	0.0167	..	..	0.0167	..	..	..	..	0.0167
Magnesium carbonate	1.0	84	0.0119	..	..	..	0.0119	..	..	..	..
Total				0.1528	0.0572	0.0855	0.0119	0.0920	0.7725	0.0806	0.1841

[1] Page 18. Published by Keramische Rundschau, Berlin, N. W., 21.

[2] A complete description of the manufacturing of this enamel and of the physical properties of a ware coated with it is given by the writer in "A Comparison of Ten White Enamels" in the *Trans. Am. Ceramic Soc.*, Vol. XIV.

[3] Molecular equivalent equals per cent. used divided by M. W.

The above total corresponds to the following molecular formula of enamel

$$\left.\begin{array}{l} 0.19\ Na_2O \\ 0.186\ K_2O \\ 0.278\ CaO \\ 0.039\ MgO \end{array}\right\} 0.399\ Al_2O_3 \left\{\begin{array}{l} 2.513\ SiO_2 \\ 0.262\ B_2O \\ 0.899\ F_2 \end{array}\right.$$

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THE PRODUCTION OF EXCESSIVE HYDROGEN SULFID IN SEWAGE DISPOSAL PLANTS AND CONSEQUENT DISINTEGRATION OF THE CONCRETE.[1]

By William M. Barr and R. E. Buchanan.

Received February 15, 1912.

It is well known to those who are familiar with the operation of the septic tank that in the chambers of such tanks, which operate in the absence of light and air, the bacteria produce, in the decomposition of the organic matter of the sewage, quantities of reducing gases. Among the decomposition products is observed more or less hydrogen sulfid gas, resulting in most cases from the decomposition of organic sulfur compounds existing in the sewage. In most tanks of this character the amount of hydrogen sulfid thus liberated is not sufficiently large to cause complaint from excessive odors or to account for the conditions in certain tanks observed by the writers.

Attention was first called to the disintegration of cement mortar in concrete resulting from sewer gases, by Olmstead.[2] The case observed by him occurred in the outfall sewer for Los Angeles, built in 1895. This resulted from the holding back of the sewage in inverted siphons in this sewer, forming, in principle, a septic tank. Beyond this point the neat cement mortar was badly disintegrated and it became necessary to reconstruct the walls and roof of this portion of the sewer. It was observed that the disintegration resulted from the formation of sulfuric acid upon the walls and roof, which attacked the cement, giving calcium sulfate as the final product. It was also observed that the amount of sulfuric acid formed appeared to be too large to have been produced by the organic sulfur compounds in the sewage proper. It was also suggested that the only possible sources of this excessive amount of sulfur were the oil wells and the sulfur which is always present in small quantities in the normal sewage. The report does not indicate that the source of these sulfur compounds was definitely located.

The case of a septic tank in England where a condition similar to the one cited above existed has been reported by Dunn,[3] but no attempt is made to show any relation between this condition and the character of the water supply.

As early as November, 1908, one of us visited the sewage disposal plant of the Inebriate Hospital at Knoxville, Iowa, and observed the following conditions: The concrete composing the roof and walls above the high water line in the dosing chamber was rapidly disintegrating. The under surface of the roof was found to be decomposed to a depth of 2 cm. Quantities of free sulfur were deposited upon the walls, and the calcium compounds of the cement were found to have been converted near the surface into crystals of gypsum. Large quantities of hydrogen sulfid were given off when the dosing chamber discharged, causing complaint of foul odors by neighbors and residents at the hospital. At a later date a similar condition was observed in the septic tank receiving the sewage of the city of Grinnell, Iowa.

In both these cases various measures have been tried to prevent the formation of excessive odors and decomposition of the concrete. A water-softening plant was installed at the Knoxville institution, thinking this might improve conditions, but, except for making the water more desirable for domestic purposes, nothing was achieved. Frequent cleaning of the tank and disinfecting at the time of cleaning did not materially improve conditions.

During the progress of this investigation our attention was called to the septic tank at the State Hospital at Mt. Pleasant, Iowa, and before visiting the place, an analysis of the water supply caused us to predict the condition existing there. A visit showed the septic tank to be in much the same condition as those first studied.

The object of this investigation was to determine the cause of the conditions above noted and to determine whether bacteria were in any measure responsible for the changes, or whether they were purely of a chemical nature. The various observations made by us, together with analyses of the water supplies and the sewage, seemed to point to some definite relationship existing between the compounds of sulfur in the water supply and the formation of excessive hydrogen sulfid, with the consequent formation of sulfuric acid on the walls of the tank.

This was used for a working hypothesis for the following reasons:

First.—The water supplies in the cases observed were found to have an unusually high content of sulfates.

Second.—The odor of hydrogen sulfid was, in all cases, very pronounced about the dosing chamber.

Third.—Free sulfur was found floating on the surface of sewage which had been standing for some time, and quantities of free sulfur were deposited on the walls in various parts of the septic tank.

Fourth.—An abundance of sulfur bacteria was evident upon microscopic examination.

Fifth.—The disintegrating concrete showed much greater amounts of sulfate than the unaffected concrete, and as already stated showed crystals of gypsum on microscopic examination.

A large proportion of proteins contain a considerable percentage of sulfur. When such compounds are decomposed in the absence of oxygen, the sulfur makes its appearance for the most part in combination with hydrogen as hydrogen sulfid. Inasmuch as proteins and the products of hydrolytic cleavage are generally to be found in sewage, it is to be expected that a certain amount of hydrogen sulfid will be de-

[1] From a Bulletin of the Eng. Expt. Sta., Iowa State College.
[2] *Eng. News*, **44**, 317.
[3] *Cement Eng. News*, **22**, 10.

veloped in such sewage as it passes through an anaërobic septic tank. The quantity so produced is not large and ordinarily little of it escapes into the air. Even in open septic tanks the heavy membrane or scum which usually forms contains many oxidizing bacteria, which may effectually prevent the escape of hydrogen sulfid. In the instances here discussed the amount of hydrogen sulfid evolved cannot be entirely accounted for by the decomposition of such protein substances, for the analyses of the raw sewage show it to be no higher in albuminoid ammonia, that is to say proteins and their decomposition products, than sewage from other disposal plants in which there is no such evolution of this gas.

The preceding table shows the amount of sulfur in the sewage calculated as SO_4 and the amount in the effluents, showing how it has been removed by reduction to hydrogen sulfid.

The investigations of various European workers, particularly Beyerinck[1] and van Delden,[2] have demonstrated that certain anaërobic bacteria in the presence of organic matter reduce sulfates to sulfids. Each of these investigators isolated specific organisms, which, when inoculated into sterile solutions containing sulfates and a little organic matter, brought about a very considerable evolution of hydrogen sulfid. It was therefore thought possible that the large amount of this gas given off in the septic tank and the dosing

ANALYSES OF RAW SEWAGE. (Figures show parts per million.)

Sample from	Nitrogen as free ammonia.	Nitrogen as albuminoid ammonia.	Chlorides.	Nitrites.	Nitrates.	Oxygen consumed.	Solids on evaporation.	Solids on ignition.
Hospital for inebriates, Knoxville, Iowa.....	21.00	6.50	35.0	none	none	53 31	3040	2484
Hospital for inebriates, Knoxville, Iowa.....	32.60	4.60	..	trace	trace	114.7	3902	2624
Grinnell, Ia., city plant.....	6.50	6.00	54.0	high	none	17.18	950	776
Grinnell, Ia., city plant.....	11.50	6.00	122.0	...	...	10.74	1114	894
Knoxville, Ia., city plant[1].....	25.00	6.00	33.0	trace	none	63.60	800	538
Ames, Ia., city plant[1].....	18.20	8.20	...	...	...	..	552	251

[1] Excessive hydrogen sulfid was not observed at these plants.

All other plants examined, where the water supply had a smaller sulfate content than that shown for the city of Knoxville in the next table, gave no excessive odor of hydrogen sulfid.

Chemical analyses of the raw sewage and effluents were made to determine the amount of sulfates in solution, and the total sulfates in the raw sewage. These results indicate, first, that the organic matter in normal sewage does not contain enough sulfur to produce the quantities of hydrogen sulfid observed; second, that where the sulfates in the original water supply are high, there is a marked reduction in the amount of mineral sulfates found in the effluent, showing that a portion of these mineral sulfates must have been reduced and removed from solution.

In three cases where excessive hydrogen sulfid was observed these relations were very marked. Several other septic tanks were observed where the sulfates in the water supply ranged from 16 to 143 parts per million as at the Knoxville city plant, and in all such

ANALYSES OF RAW SEWAGE.

Source of sample.		Total sulfur as SO_4.	Soluble sulfur as SO_4.
Inebriate Hospital, Knoxville, Ia.....	Water supply	1664	1664
Inebriate Hospital, Knoxville, Ia.....	Softened water	1566	1566
Inebriate Hospital, Knoxville, Ia.....	Raw sewage	1552	1533
Inebriate Hospital, Knoxville, Ia.....	Tank effluent	..	965
Grinnell, Ia.....	Water supply	476	476
Grinnell, Ia.....	Raw sewage	452	427
Grinnell, Ia.....	Tank effluent	381	352
State Hospital, Mt. Pleasant, Ia.....	Water supply	900	900
State Hospital, Mt. Pleasant, Ia.....	Raw Sewage	871	850
State Hospital, Mt. Pleasant, Ia.....	Tank effluent	716	690
Knoxville, Ia.....	Water supply	143	143
Knoxville, Ia.....	Raw sewage	163	147
Knoxville, Ia.....	Tank effluent	..	145

cases very little hydrogen sulfid could be detected at the tank. The Knoxville city plant shows the highest sulfates in the raw sewage of any plant observed where excessive hydrogen sulfid did not appear, and it is doubtful whether this amount of sulfates might not cause trouble in some cases.

chamber might be due in large part at least to a reduction of the sulfates of the water supply. The chemical analyses of these waters show them to be exceptionally high in sulfates. Tests were accordingly made to determine whether or not such sulfates under the septic conditions of this plant would be transformed into sulfids.

The following solutions were prepared in two liter lots, and 500 cc. placed in each of four liter flasks, the solutions in each case being covered by a layer of neutral paraffine oil. This furnished anaërobic conditions for bacterial growth, inasmuch as paraffine oil permits little or no oxygen to penetrate it. After sterilization three of each set of the flasks were inoculated, one being retained as a check. The material used in inoculation was secured from different parts of the septic tank and the dosing chamber of the plant at the Inebriate Hospital at Knoxville. After inoculation the flasks were kept in the laboratory at a temperature of about 18°C.

COMPOSITION OF MEDIA USED

Material.	Sol. 1.	Sol. 2.	Sol. 3.	Sol. 4.	Sol. 5.	Sol. 6.
Tap water.....	1000 cc.	1000 cc.	1000 cc.	1000 cc.	1000 cc.	1000 cc.
NaCl.....	30 g.	...	...	...	..	...
K_2HPO_4.....	0.5 g.	0.5 g.	0.5 g.	0.5 g	0.5 g.	0.5 g.
Asparagin.....	1.0 g.	1.0 g.	1.0 g.	1.0 g.	1.0 g.	1.0 g.
$MgSO_4$.....	8.0 g.	8.0 g.	...	...	...	2.0 g.
Na_2SO_4.....	...	...	2.0 g	4.0 g	10.0 g.	...
$FeSO_4$.....	0.1 g.	0.1 g.	0.1 g.	0.1 g.	0.1 g	0.1 g.

The iron in each of the above solutions was added as an indicator. The formation of sulfid was shown by the deposition of black iron sulfid.

Within two or three days the solutions 2, 3, 4, 5 and 6, almost without exception, began to turn gray and within two weeks an abundant precipitate of iron sulfid was visible in all. It is evident, then, that bacteria having the power to reduce sulfates to sulfids were present in numbers in the sewage in question. The quantity of sulfate daily entering the plant justifies

[1] *Cent. für Bakt., 2nd abt.*, **1**, 1, 49, 104 (1895)
[2] *Ibid.*, **11**, 81, 113 (1903).

the conclusion that much of the hydrogen sulfid developed in the tank is formed by the deoxidation of such sulfates.

Stained mounts were prepared at intervals from each of the flasks described above. At first no bacterial type or organism appeared to predominate; large and small bacilli, cocci, and a few spirilla were present. At the end of the two weeks most of the flasks showed a decided predominance of spirilla. Those containing the highest percentage of hydrogen sulfid were practically pure cultures of this organism.

A medium of the same composition as solution 5 described above, with the addition of 1.5 per cent. agar agar, was used for the purpose of isolation. Different dilutions were plated and the medium covered with paraffine to exclude oxygen. In three or four days black specks appeared in the plates, the areas of discoloration often reaching 10 mm. by the end of the week. Near the center of such areas could be observed small opaque colonies, generally considerably less than 1 mm. in diameter. These colonies were found to consist of the characteristic spirillum noted above. When grown in test tubes containing solution 5 under anaërobic conditions, pure cultures were found to produce a rapid reduction of sulfates to sulfids.

It may be concluded that in the particular sewage of the Knoxville Hospital, this spirillum alone is capable of producing hydrogen sulfid in quantities sufficient to account for the amount present in the dosing chamber and septic tank.

Zelinsky,[1] in 1893, described a motile elongated bacillus (Bacillus Hydrosulfurōum ponticum) obtained at considerable depth from the ooze of the Black Sea. This organism under anaërobic conditions was found to reduce sulfates and sulfites to sulfids.

Beyerinck[2] isolated a specific organism (Spirillum desulfuricans) from canal water. Inoculation of this organism into media containing sulfates resulted in the rapid development of sulfids. Morphologically the organism was from one-half to a full spiral, rather rarely the latter. In the absence of oxygen it is actively motile. It is probable that the organism isolated from the sewage disposal plant at the Knoxville Hospital is the same as the one described by Beyerinck.

Van Delden[3] made a further study of the S. desulfuricans of Beyerinck and also described the form Microspira aestuarii from near the mouth of one of the Holland rivers. The ooze at the bottom of the sea in such places was found to be blackened by sulfids. He made an extensive study of the reduction of sulfur compounds by these organisms in both pure and mixed cultures. M. aestuarii he found to be the more efficient of the two as a reducing agent, producing in the course of seven weeks as much as a gram of hydrogen sulfid per liter of water. Morphologically this organism resembles the former very closely.

Examination of the dosing chambers of the tanks observed showed that the moisture on the walls was strongly acid with sulfuric acid. A considerable portion of this acid was doubtless produced by atmospheric oxidation of the hydrogen sulfid, which of itself might account for the formation of the sulfuric acid and the sulfates found in the concrete. The bacterial study, however, shows another agent which aids materially in the oxidation of the hydrogen sulfid.

The work of Winogradsky, Engelman, Miyoshi, and others has shown that certain groups of bacteria under aërobic conditions may utilize hydrogen sulfid by direct or indirect oxidation as a source of energy. The first evidence of such oxidation is frequently the accumulation within the bacterial cell of granules of free sulfur. These may be recognized microscopically by their relatively high refractive index, by their solubility in carbon disulfid and by the characteristic crystals which form when such solutions are allowed to dry upon a glass slide. These organisms are found later to further oxidize this free sulfur, the final product being sulfuric acid. The organic food requirements of these bacteria seem to be very small; indeed, many apparently utilize the carbon dioxide of the atmosphere and very simple compounds of nitrogen.

In examination of the septic tanks in question one of these oxidizing sulfur organisms (Beggiatoa) was found growing abundantly in some places on the surface of the scum. Disintegrating concrete, moreover, was covered by a luxuriant growth of moulds and bacteria. A comparison of the chemical analysis of sound concrete, and that which has undergone partial disintegrations, hows a notable increase in the amount of sulfate present in the latter. It should be noted further that the concrete below the water line of the septic tank and dosing chamber had disintegrated little or none at all. It seemed evident, therefore, that hydrogen sulfid alone could not be the immediate cause of such disintegration, for it is constantly present in the sewage in contact with those walls. Inasmuch as bacteria, however, seemed to thrive in the moisture generally present on the under side of the roof and on the walls, it seemed probable that much of the hydrogen sulfid arising from the sewage is absorbed and then converted into sulfuric acid through the agency of bacteria.

ANALYSIS OF DISINTEGRATED CEMENT WALL IN SEPTIC TANK AT GRINNELL, IOWA, SHOWING VARIATION IN SULFUR CONTENT OF DIFFERENT PARTS OF CONCRETE.

	Free sulfur.	Sulfates (SO_4).
First or outer[1] layer, 1/4-inch thick.....	19.7%	1.2%
Second layer, immediately beneath first....	7.2	21.0
Third layer, one inch below surface.....	0.27	6.75

One hundred cm. flasks containing various sulfids were inoculated with material from the disintegrated concrete and examined from time to time. In some of these flasks Beggiatoa filaments developed, showing their characteristic sulfur granules within the cells. However, active oxidation of the sulfids to sulfates occurred in the other flasks in the absence of Beggiatoa, apparently through the agency of other bacteria which swarmed in such cultures.

The following solution was prepared to determine definitely whether or not such bacteria were actually

[1] *Proc. Rus. Phys. Chem. Soc.*, Fasc. 5.
[2] *Loc. cit.*, **1895.**
[3] *Loc. cit.*, **1903.**

[1] This layer consisted chiefly of a deposit of free sulfur.

capable of oxidizing sulfids to sulfates. Freshly precipitated, chemically pure iron sulfid and calcium carbonate were added in equal amounts in 100 cc. flasks. To each of these flasks was then added 5 cc. of Knop's solution and after sterilization five were inoculated, the remainder being retained as checks. Within a week the inoculated solutions became cloudy, the uninoculated remaining clear. Stained amounts showed the presence of a capsulated rod showing polar staining in all inoculated flasks. This organism was present in all these flasks in practically pure cultures. Comparative analyses of the contents of the check and of these flasks showed that in those in which bacteria had been developed, between two and three times as much sulfate was present as in the check. The presence of this organism in the solution undoubtedly was the cause of the rapid oxidation of the sulfids which took place. However, the organism has not as yet been isolated in pure cultures and quantitative studies made of its oxidizing power.

The data at hand are sufficient to convince us that bacteria may be responsible, in part at least, for the oxidation of sulfids to sulfates under the conditions as they exist in the sewage disposal plants here discussed.

As rapidly as sulfuric acid is produced by bacteria working in and on the concrete or by atmospheric oxidation, it reacts with the calcium compounds of the cement, forming calcium sulfate. This takes up water of crystallization and swells considerably, the result being a cracking and pulverizing action and a consequent disintegration.

Careful search has failed to reveal any account of bacterial disintegration of concrete through the action of sulfids or sulfates. R. Grieg Smith[1] investigated the disintegration of concrete in the open canals that convey the city water supply of Sidney, New South Wales. He was led to study the action of nitrifying bacteria on concrete through the work of Stutzer and Hartleb, who suggest that such forms might assist in the disintegration of the cement of water reservoirs. He concludes, however, that "there is considerable room for doubt regarding the action of microörganisms on cement. There is more reason to believe that the action is purely chemical." His conclusions would seem to agree with those of Tannatt and Burke,[2] who found disintegration of concrete tile to take place when in contact with soil rich in sulfates. That even in alkali regions bacteria may have something to do with concrete disintegration is evidenced from the work here recorded and the statement of Schreiner, Oswald and Failyer[3] to the effect that hydrogen sulfid is produced in the drainage waters from gypsum alkali lands and from iron pyrites.

SUMMARY.

1. In three of the sewage disposal plants observed, *viz*: Grinnell, State Inebriate Hospital, and State Hospital at Mt. Pleasant, large quantities of hydrogen sulfid are evolved. This sulfid is produced in two ways: (*a*) by the bacterial decomposition of sulfur containing proteins and related compounds, and (*b*) by the reduction of sulfates which are contained in unusual amounts in the water supplies used. Of the two the second seems to be the more important.

2. The organism chiefly responsible for the reduction of sulfates and evolution of hydrogen sulfid is a spiral bacterium closely related to, if not identical with, *Spirillum desulfuricans*.

3. The hydrogen sulfid which escapes as gas from the sewage, particularly in the dosing chamber, is partially dissolved in the moisture on the under side of the roof and concrete walls. Here it is oxidized to sulfuric acid partly by atmospheric oxidation and partly by bacterial action. The sulfuric acid acts upon the calcium compounds of the concrete forming calcium sulfate, and breaking down the concrete. There is often deposited an excess of free sulfur which the oxidizing agencies have not converted to sulfate.

4. The exact species of the organisms responsible for the conversion of hydrogen sulfid into sulfuric acid have not been determined. That bacteria, however, in mixed cultures may bring about this change has been demonstrated. Beggiatoa and a bacillus have been isolated and are probably the most important organisms in bringing about this change.

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[1] *Cent. f. Bakt., 2nd Abt.*, **8**, 377 (1902).

[2] "The Effect of Alkali on Portland Cement," Bull. Mont. Agr. Exp. Sta., 1908.

[3] Bull. U. S. Dept. Agr., Bur. of Soils, 1906.

MARKING PORCELAIN AND SILICA CRUCIBLES, ETC.[1]

By P. A. YODER.

Received April 4, 1912.

INTRODUCTION.

In the analytical laboratory there often is occasion to put upon crucibles, etc., permanent distinguishing marks which will stand ignition and mild treatment with acids and alkalis. The blue pencil or the brush and china paints which are frequently used for this purpose, the markings being burned in, often give results so crude as to be quite unsatisfactory, especially for articles that are before one's eyes daily for years. Moreover, the blue-pencil marks and many china colors lack permanence, and when applied to silica wares do not adhere satisfactorily. The writer has worked out two methods, one for marking with platinum and the other for the application of china paints, both by the use of rubber type.

THE PLATINUM PROCESS.

The crucibles are cleaned by heating for half an hour with nitric acid, one part concentrated acid to one part of water. A sizing is prepared consisting of a hot 5 per cent. solution of gelatin. The parts of the crucibles to be marked are dipped into this sizing and set aside to drain and dry. When the gelatin is dry, the desired number is stamped on with a solution of platinic chlorid containing 12 to 15 per cent. of platinum—*i. e.*, about 32 to 40 per cent. of the hydrated, crystallized chloroplatinic acid. The pad holding the solution may be made of six or eight folds of smooth linen or muslin and need not be much larger than the type used. This pad is nearly

[1] *Circular* **93**, Bureau of Chemistry, United States Department of Agriculture.

saturated with a few drops of the platinic chloride solution. Too much of the solution causes blurring and too little of it or too dilute a solution results in dim numbers. After the numbers are dry the crucibles are gently heated until the platinum is reduced and the gelatin burned off. This is most conveniently accomplished in a muffle. Finally, the numbers are heated for one-half minute in the flame of the blast lamp—*i. e.*, for one-half minute from the time it attains the temperature of the flame.

If the wares are cleaned and fired as directed, the markings adhere well. The figures become more prominent if burnished by use of a china painter's burnishing stone, if available, or of seashore sand, or less advantageously of a silica soap. The deposit is resistant to single acids, but not to alkalis. In some experiments library paste was substituted with good results for the gelatin sizing. Gold and mixtures of gold and platinum solutions may be applied similarly, but there is more danger of volatilizing the gold chloride before reduction takes place, and thereby causing a spreading of the deposit. The resulting figures also are less conspicuous than when platinum is used. This method of getting the deposit of platinum or gold may possibly find use also in decorating chinaware. If the solution is applied with a brush, a quill, or a glass stylus, it may be more dilute. The same method applied to silica wares also gives very satisfactory results.

APPLICATION OF CHINA COLORS BY USE OF RUBBER STAMPS.

Paints mixed in oil are not satisfactory for use with rubber stamps because the type leaves on the porcelain a rim of thickened paint while the main surface of contact is relatively bare. The method finally adopted is to stamp the wares to be marked with a sizing or varnish similar to that which painters use for applying gold leaf. "Fat oil"—*i. e.*, partly oxidized linseed oil, supplied by paint dealers—proved very satisfactory for this purpose. While this sizing is still sticky, the dry pigment is dusted on with a camel's-hair brush. After the varnish has set, the excess of pigment is wiped off and the crucible is fired at a strong red heat, preferably in a muffle. The "fat oil" dries slowly. This is an advantage because then some time may be allowed between its application and the dusting on of the pigment, for the irregular layer on the porcelain to draw out by surface tension into a smoother one. Standing over night at room temperature, or for one hour in a drying oven at 100° C., suffices for the varnish to set. The pad used for "inking" the type may consist of several thicknesses of linen cloth and is nearly saturated with this varnish. Too much varnish on the pad must be avoided, as it results in figures with ragged outlines. This varnish may readily be cleaned from the rubber type, before it has set, by use of a 10 per cent. alcoholic solution of caustic potash applied with a small bristle brush.

COLOR TESTS.

Seeking a prominent color and one resistant to both acids and alkalis, a series of tests was made with samples of overglaze blues, blacks, and reds supplied by a dealer and one blue prepared by the writer. These were stamped onto porcelain crucibles as above described. The heat used in firing was a red heat slightly lower than that at which the colored figures on the white background disappeared (the radiation plus reflection from a colored surface equaling that from a white surface). In one test they were brought from a dull red to the above temperature during the course of one hour and then cooled. This sufficed to make the blacks and the reds resistant to nitric acid (35 per cent.) and to sodium hydroxide solution (10 per cent.), but the blues were appreciably soluble in the acid. To make the blues resistant, they had to be fired to a higher temperature or held at the above maximum temperature for about an hour. To test the permanence of the markings, the acid and the alkali were each applied five minutes cold, followed by five minutes at a boiling temperature. Of the seven blacks tried, two—*viz.*, a lettering black and a blue black—gave especially good effects in that they yielded a very strong black. Of the same samples when applied to silica dishes and fired as indicated, both the blacks and the reds were again resistant to both nitric acid and alkali, but the blues, even when fired more strongly, came off very readily in nitric acid.

In these tests an electric muffle was used. In heating porcelain crucibles to a high temperature in gas muffles in which the muffle chambers were not thoroughly sealed off from the gas chambers, and occasionally also in the electric muffle, a brown stain developed on the porcelain. This could readily be removed by heating the crucible half a minute in the blast flame, most conveniently in a suitable chimney.

In applying the rubber stamp to the crucibles it is difficult to avoid a sliding motion that blurs the imprint. This may be prevented by using a suitable guide or a steadying support. The writer found it convenient to rest both the inverted crucible and the type holder on a smooth surface while making the impression. In numbering crucibles, etc., it is often advantageous to have the number on three sides so as to make it visible, no matter which way the crucible is turned.

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ON THE QUANTITATIVE ESTIMATION OF SODIUM HYDROXIDE IN "BLACK LIQUOR."

By EDWIN SUTERMEISTER AND HAROLD R. RAFSKY.

Received January 16, 1912.

In the manufacture of cellulose by the soda process wood is digested under pressure with a solution of sodium hydroxide. The liquid separated from the resulting pulp is called "black liquor," and contains the sodium hydroxide unconsumed in the reaction, together with the sodium salts of acids formed by the decomposition of the wood. A precise evaluation of this residual sodium hydroxide would give valuable information on the exact consumption of caustic soda

by wood, and perhaps help to explain the chemistry of the digestion process.

PRESENT METHOD.

The method now employed is simply one of titration with acid, using a solution of phenolphthalein as an outside indicator.[1] In detail: 25 cc. of black liquor are diluted with 300 cc. of water; 10 cc. of a concentrated $BaCl_2$ solution (400 grams to liter) are added to precipitate carbonates and the organic acid radicles which yield insoluble barium salts, and the solution is titrated with N acid (HCl, HNO_3 or H_2SO_4). The end point is determined by removing drops of the solution at intervals during the titration and allowing them to fall gently from a stirring rod into a solution of phenolphthalein in water just covering the bottom of a beaker. When a drop fails to develop a red color in the indicator solution immediately surrounding it, the end point is considered to be reached. This method is approximate only, but checks within 5 per cent. can generally be obtained; *e. g.*, three successive titrations required respectively 5.00, 4.90, 5.11 cc. *N* acid.

The difficulties in arriving at the end point are: first, the distinguishing of the red color of the indicator from the brown of the drop; and, second, the slow development of the red color around the drop. The real trouble, however—dependent, perhaps, on the two just mentioned—is that the end point recorded varies with the working conditions. Thus if the titration is carried out at dilutions other than the one given above, widely differing values are obtained, as is shown in the following table which gives the results of titrating 25 cc. of black liquor at different dilutions:

Total vol. of diluted black liquor.	Individual titrations. N acid.	Average.
39 cc.	3.50 cc.	3.46 cc.
	3.42 cc.	
88 cc.	3.67 cc.	3.63 cc.
	3.60 cc.	
185 cc.	3.56 cc.	3.62 cc.
	3.70 cc.	
	3.60 cc.	
435 cc.	4.13 cc.	4.45 cc.
	4.62 cc.	
	4.30 cc.	
	4.74 cc.	
835 cc.	5.00 cc.	5.00 cc.
	4.90 cc.	
	5.11 cc.	
1635 cc.	4.92 cc.	5.03 cc.
	5.15 cc.	

Again, if there is added to a black liquor (which has been analyzed by the present method) a known amount of NaOH and this "fortified" black liquor is then titrated, the increase of acid used in titration is smaller than the amount equivalent to the NaOH added. For instance: to a black liquor titrating 6.39 cc. acid, NaOH was added equivalent to 8.28 cc. acid, and duplicate titrations of this "fortified" black liquor showed readings of 13.54 and 13.64 cc., an average of 13.59 cc., while the calculated result is 14.67 cc.

One possible explanation of these inconsistencies is that the OH ions are adsorbed by the colloids present. Another theory supposes the presence of an organic complex which combines with OH ions, the resulting molecule having but a small dissociation constant. On increasing the concentration of OH ions (as in a "fortified" black liquor) the dissociation is checked, whereas a decrease in the concentration of OH ions (as in dilution) increases the dissociation and hence the total amount of OH ions present.

[1] For the basic idea involved in this method we are indebted to Mr Chas. N. Waite, of Wilmington, Del.

ATTEMPTS TO IMPROVE PRESENT METHOD.

The following is a description of numerous attempts to improve our original method, and is published in the hope of bringing forth some more successful method, or of starting a discussion and stimulating further work along this line.

Preliminary Experiments.—Small test tubes, partly filled with a solution of phenolphthalein in water, were tried for the examination of the individual test drops, but no satisfactory end point was obtainable. The idea of using phenolphthalein directly in the solution to be titrated, after the addition of a white substance such as $BaSO_4$ or China clay to lighten the color, proved a failure as the color change was gradual and indefinite.

Elimination of Precipitate.—We next sought to eliminate the voluminous precipitate produced on addition of $BaCl_2$, in order to obtain a clear liquid for titration. Ordinary settling, filtration, and centrifugal filtration proved unsatisfactory, but in a Babcock centrifuge a clear orange colored solution was secured by adding clay to the regular titration mixture and centrifuging for 7 or 8 minutes. This clear liquid when poured off and titrated with phenolphthalein directly did not give very close duplicates, *e. g.*, 13.76 and 14.64 cc. $N/10$ HCl.

Indicators Tried.—As we were unable to decolorize the clear centrifuged solution with charcoal, we directed our attention to procuring a better indicator. Litmus, Congo red, and lacmoid, with blue-red or red-blue color change were unavailable as the orange color of the solution interfered with the end point. A mixture of dyes, the color of which was practically complementary to the orange shade, was added in an attempt to produce a gray—so that an indicator could be used to better advantage—but the dyes changed color, owing to the action of the alkaline solution, and satisfactory results were not obtained. A mixture of phenolphthalein and malachite green showed some promise but was finally discarded as the malachite green when used in sufficient amount to cover the orange color tended both to precipitate in neutral solution and to mask the last traces of the red of the phenolphthalein. We found, however, that by using an *excess* of phenolphthalein alone we arrived at a satisfactory and definite end point. Our method was to add a few drops of indicator, titrate to disappearance of red, add a large excess of indicator, and again titrate to the disappearance of red, repeating this operation till no red color developed on addition of more indicator.

Determination of Ratio.—Up to this point we were titrating a portion of the clear liquid obtained by precipitating the black liquor with $BaCl_2$ and centri-

fuging. It now became necessary to determine the ratio of the NaOH in the portion used to that in the entire volume of clear liquor and precipitate.

The first method attempted was to find the total amount of NaOH present in the entire mixture (20 cc. $BaCl_2$, 50 cc. black liquor, 20 grams clay, and 175 cc. of water) by titrating the entire quantity of centrifuged liquor in the usual way and then repeatedly extracting the sludge with water, and centrifuging till the final extraction gave no test with phenolphthalein. As the total volume of the solution was too large to work with conveniently, one-fifth was taken. This idea worked well until the third extraction with water when the clay did not drag down the sludge, but left it in suspension making titration impossible. Addition of more clay was of no avail, and consequently as the sludge still reacted strongly alkaline, the method was abandoned.

The problem was next attacked on the theory that if a known amount of NaOH were added to a black liquor and the mixture centrifuged as usual the same percentage of the added NaOH as of that originally present would be found in the clear liquor. Having determined what percentage of the added NaOH was present in the centrifuged liquor titrated we could then calculate the total amount of NaOH present in the original sample of black liquor.

With this basic idea, we made up the following two mixtures: 25 cc. of black liquor, 10 grams of clay, and 50 cc. of $BaCl_2$; and 25 cc. of black liquor, 10 grams of clay, 45 cc. of $BaCl_2$ and 5 cc. NaOH (= 48.80 cc. $N/5$ HCl). These were centrifuged under the same conditions and 10 cc. of each of the centrifuged liquors titrated. The first titration (2.12 cc. $N/5$ HCl) represented the amount of NaOH present from the black liquor; the second (8.80 cc. $N/5$ HCl) the amount of NaOH present from the black liquor plus added NaOH. Thus the added NaOH present in the 10 cc. of centrifuged liquor = 8.80—2.12 = 6.68 cc. $N/5$ HCl. The percentage of the total added NaOH present in the 10 cc. of centrifuged liquor $= \frac{6.68}{48.80} = 13.7$ per cent.

According to the above theory only 13.7 per cent. of the NaOH present in the original black liquor is to be found in 10 cc. of the clear centrifuged liquor and as this 13.7 per cent. is represented by 2.12 cc. $N/5$ acid the total amount of NaOH present would be equivalent to 15.48 cc. $N/5$ or 3.09 cc. N acid. A series of similar tests were made of which the following is a summary: two determinations of pure black liquor, carried out in the manner outlined above, gave as titrations for 10 cc. of the centrifuged liquor 2.14, 2.10, and 2.19, 2.14, 2.12 cc. $N/5$ acid; average, 2.14 cc. $N/5$ HCl. The table below gives the results of four tests on "fortified" black liquors, *i. e.*, black liquors to which NaOH has been added. All figures given, except the last column, indicate $N/5$ acid used.

The average of the four values found below is 3.14 cc. N HCl for the titer of 25 cc. of black liquor. The peculiar part, however, for which we can assign no reason is: that by titrating according to our original method we get a value of from 6–7 cc. N acid for the titer of the same volume of black liquor. Until we can explain why this discrepancy occurs, we cannot proceed further with this method.

	Titration 10 cc. centrifuged fortified black liquor.	Value of NaOH present from black liquor.	Value of NaOH present from added NaOH (I-II)	Value of total NaOH added.	Per cent. total added NaOH present in 10 cc. centrifuged liquor (III) / IV	Calculated value of NaOH in original black liquor $\left(\frac{III}{V}\right)100$	NaOH value of original black liquor in terms of N acid.
1.....	8.82 8.79	2.14	6.66	48.80	13.65	15.68	3.14
2.....	8.71 8.67	2.14	6.55	48.80	13.42	15.94	3.19
3.....	15.45 15.45	2.14	13.31	97.60	13.63	15.70	3.14
4.....	22.55 22.54	2.14	20.40	146.40	13.92	15.37	3.07

Average = 3.14 cc. N acid

Electrometric Method.—A problem very similar to the one at hand, *i. e.*, the determination of the acidity of tan liquors, has reached a successful solution by the employment of the electrometric method of titration, as reported by Sand and Law[1] and by Sand, Law and Wood.[2] They measure the voltage of a cell, one arm of which is a normal calomel electrode, and the other a hydrogen electrode dipping into the tan liquor to be titrated. Acid is added to the tan liquor until a potential of 0.69 volt is registered, which indicates neutrality.

Through the kindness of Dr. Geo. S. Forbes, of Harvard University, one of the writers was permitted to use apparatus and space in his laboratory to test out this method. We are also indebted to Dr. Forbes for much valuable advice and assistance. The work reported below was carried out very roughly, the object being merely to test the applicability of the method for our use. Our apparatus consisted of a cell similar to that employed in the tan liquor determination, the potential of which was measured by the compensation method using a potentiometer box. We employed a D'Arsonval galvanometer and although this tended to polarize the hydrogen electrode, for approximate work it proved more convenient than an electrometer.

As we were uncertain as to the magnitude of a possible reducing action of black liquor on the hydrogen electrode, we could not assume that the potential corresponding to a given concentration of a pure NaOH solution would necessarily indicate the same concentration of NaOH in the black liquor solution. To test this point we titrated a black liquor according to our original method to get the approximate concentration of NaOH; then we made up a pure NaOH solution of similar concentration (0.026 N), and read off the potentials of the two solutions in the cell.

[1] *J. Soc. Chem. Ind.*, **30**, 1, 3.
[2] *Ibid.*, **30**, 14, 872.

Calculated potential	1.00 volt
Black liquor	0.97–0.98 volt
Alkali	0.99 volt

The above potential in the alkali, and especially in the case of the black liquor, was not reached for several minutes.

Another determination of a solution one-tenth as strong, 0.0026 *N*, gave a voltage of 0.91 in the black liquor. The calculated voltage is 0.94.

Both the above determinations indicated that the reducing action of the black liquor did not greatly affect the hydrogen electrode in alkaline solution so we next tried the direct titration of the black liquor.

For this purpose we took 25 cc. black liquor, 10 cc. $BaCl_2$ (400 grams to liter), and 200 cc. water. A similar mixture by our old method titrated 13.1 cc. *N*/2 acid. The first titration registered no sudden fall of potential but rather a steady diminution of voltage up to 28.6 cc. acid (as much as was added) and a second trial resulted similarly. When, however, about 10 cc. concentrated HCl was added, the colloids coagulated and the voltage dropped to 0.33.

To make certain that the H electrode had not been affected by its immersion in the black liquor, immediately after the above titration it was placed in a neutral KCl solution and the voltage found to be above 0.6 volt. In contrast with the black liquor titration above, at the neutral point in the titration of an NaOH solution, as indicated by phenolphthalein, the addition of an extra quarter cc. of *N*/2 acid causes a very sharp diminution of the potential of the cell. From the determinations given above we concluded that the electrometric method was, as applied, inapplicable in our case.

SUMMARY.

The present method for the determination of NaOH content of black liquors is one of titration with acid, using phenolphthalein as an outside indicator.

In the attempt to improve this method, the more important ideas worked upon were:

1. The elimination by centrifugal action of the precipitate formed by $BaCl_2$ and the subsequent titration of the clear liquor.

2. The use of various indicators, and the successful method of employing phenolphthalein.

3. The determination of a ratio between the centrifuged liquor and the sample of black liquor taken.

4. Electrometric method.

None of the methods or modifications thus far tested has proved entirely satisfactory, and the original method, although it gives only approximate results, is the best one at present available.

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THE CHEMISTRY OF ANAESTHETICS, IV: CHLOROFORM.

By CHARLES BASKERVILLE AND W. A. HAMOR.

Received December 12, 1911.

(Concluded from July No.)

VIII. The Examination of Anaesthetic Chloroform.

10. THE DETERMINATION OF THE ACIDITY OF CHLOROFORM.

Chloroform of all grades should always be examined for the presence of acids.[1] In this way it may be ascertained whether the chloroform under examination has been purified by a method serving to eliminate any acids resulting during manufacture or used during purification; if in a tin container, whether the proper care has been exercised in capping; and, since the water extract is usually tested, the extent of any oxidation, either of alcohol or chloroform, may be determined.

The *Codex Medicamentarius Hamburgensis* of 1847 required that anaesthetic chloroform (density 1.48) should not afford a water extract possessing an acid reaction towards litmus. This test has met with general favor, and is essentially the one usually recommended.[2]

It has been proposed, however, that the chloroform be allowed to evaporate spontaneously after the addition of a drop of neutral litmus solution;[3] and that pieces of pith steeped in Congo red solution be used for the detection of acids in chloroform.[4]

Vulpius[5] found that several chloroform samples which satisfied the conditions of the silver nitrate[6] and litmus paper tests showed an acid reaction when treated as follows: To 1 cc. of water, 1 drop of phenolphthalein solution and 1 drop of centinormal potassium

[1] The possible contaminants of this class are: hydrochloric, hypochlorous, sulphuric, acetic and formic acids; of these, however, only hydrochloric and acetic acids are probable now. There are cases on record which indicate that samples of chloroform may sometimes contain free hydrochloric acid; in all such instances, all of which are extreme in the case of anaesthetic chloroform, either the chloroform originally contained no preservative or had been very carelessly stored for protracted periods of time.

[2] Acids, free chlorine and chlorides are all extracted from chloroform by water, so that when the sample is shaken with, say, twice its volume of water for about 5 minutes, free acids may be detected, when present in appreciable amounts, by blue litmus paper. The detection of the products of the oxidation of pure chloroform will be referred to specifically in the next section.

Brown (*Pharm. J.*, [3] **25,** 865) stated that a water extract of the chloroform under examination should be neutral to litmus; Gay (*Loc. cit.*) recommended that when 6 cc. are shaken with 3 cc. of water, the water extract should not redden litmus paper; Regnault (*Mon. Sci.*, [3] **5,** 417) also recommended that chloroform should be neutral ro litmus; White (*Pharm. J.*, [4] **25,** 540) directed that 5 mils be agitated with 10 mils of water, and that the water layer stand the test with litmus; and Krauch (*Testing of Chemical Reagents*, **1902,** 77) gives a test wherein 2 parts of chloroform are shaken with 3 parts of water, the latter being then tested with blue litmus paper. See also Linke, *Apoth.-Ztg.*, **25,** 285.

The pharmacopoeias of Spain and France require that chloroform shall be completely neutral to litmus solution; the pharmacopoeias of Switzerland and Austria direct that the chloroform be agitated with an equal volume of water, and that the latter should then not redden litmus or be rendered turbid by silver nitrate solution, while the Danish pharmacopoeia directs that the test be made on the aqueous extract obtained by agitating 10 cc. of chloroform with 5 cc. of water. Practically the same test recommended in the *Codex Medicamentarius Hamburgensis* of 1847 is in the *Deutsches Arzneibuch* of 1910. The *Pharmacopoeia of Japan* of 1907 requires that the sample be shaken with one-half its volume of water, and that the aqueous extract should not redden blue litmus paper. It was specified in the sixth revision of the *Pharmacopoeia of the United States* (1882) that if 5 cc. of purified chloroform be thoroughly agitated with 10 cc. of distilled water, the latter, when separated, should not affect litmus paper (blue).

[3] It was required in the fifth revision of the *Pharmacopoeia of the United States* (**1873,** p. 78) that when 1 fluidrachm of chloroform was evaporated spontaneously with 1 drop of a neutral water solution of litmus, the color of the indicator must not be reddened; it was stated that the result of the test is the same if the chloroform, contained in a white glass bottle, had been previously exposed to direct sunlight for 10 hours. A similar test is given in the *National Dispensatory* of **1887** (p. 439) for incipient decomposition.

[4] A change to "blue" results in the presence of acids. Concerning this test, see *Lancet*, **1907,** I, 1033.

[5] *Arch. Pharm.*, [3] **25,** 998.

[6] This test will be discussed in the next section.

hydroxide solution were added, and the whole was shaken with 5 cc. of the chloroform. In four cases the solution was decolorized in two minutes. On the addition of a second drop of the potassium hydroxide solution, decolorization again occurred, and with one sample this was the case after the addition of two more drops of the alkali.[1] Accordingly, Vulpius suggested as a further check on the purity of chloroform that 10 cc. repeatedly shaken in a stoppered bottle it nearly fills with 2 cc. of water colored with 2 drops of phenolphthalein solution, and 1 drop of decinormal potassium hydroxide solution should not decolorize the latter in 24 hours.[2]

We have found that when 20 cc. of *pure* anaesthetic chloroform are thoroughly agitated with 10 cc. of water and 2 drops of phenolphthalein solution, and then titrated with $N/100$ potassium hydroxide solution, added drop by drop, 0.10 cc. of the standard alkali produces a temporary alkaline reaction; but the dissociation of the phenolphthalein alkali is retarded, and the red color disappears on agitation, 0.2 cc. of $N/100$ potassium hydroxide being required to produce a faint, yet decided, alkaline reaction permanent for 15 minutes, when the mixture is shaken 30 seconds after the addition of each drop of alkali.

The following results were obtained with various samples of chloroform:

Description.	U. S. P. test for acidity.	Cc. $N/100$ KOH required as by above test.	Gms. acid, calculated as acetic, per 100 cc. of sample.
A. Salicylid-chloroform; 0.25 per cent. alcohol	Negative	0.2 cc.	None
B. "Chloroform purified;" 0.5 cc. absolute alcohol in 100 cc.	Negative	0.3 cc.	0.0003 g.
C. "Chloroform medicinale Pictet"	Negative	0.2 cc.	None
D. "Purified chloroform;" of full U. S. P. quality	Negative	0.25 cc.	0.00015 g.
E. "Chloroform e chloral," "absolutely pure;" 0.3 cc. absolute alcohol in 100 cc.	Negative	0.25 cc.	0.00015 g.
F. "Chloroform pure;" 0.56 cc. absolute alcohol in 100 cc.	Negative	0.20 cc.	None
G. "Chloroform, U. S. P.;" 0.7 cc. absolute alcohol in 100 cc.	Negative	0.20 cc.	None
H. A 5 lb. unopened tin of chloroform, supposed to be of U. S. P. quality, but 17 mo. old	Negative	0.35 cc.	0.00045 g.
I. A 125 cc. tin of "chloroform for anaesthesia," six years old	Negative	0.50 cc.	0.0009 g.
J. A tin containing 6 ounces of "chloroformum purificatum," made in 1863 or shortly before	Negative	0.35 cc.	0.00045 g.
K. A sample of anaesthetic chloroform prepared by the manufacturers of I; conforming with all the requirements of the U. S. P. but the sulphuric acid test	Negative	0.25 cc.	0.00015 g.
L. "Purified chloroform," prepared from carbon tetrachloride; 0.74 cc. absolute alcohol in 100 cc.	Negative	0.20 cc.	None
M. "Purified chloroform, U. S. P.;" 0.8 cc. absolute alcohol in 100 cc.	Negative	0.30 cc.	0.0003 g.
N. "Commercial chloroform," the source of M	Negative	0.25 cc.	0.00015 g.

We have been led to conclude that—

(*a*) Whereas litmus is sufficiently sensitive for use in the detection of hydrochloric acid in chloroform,[3] phenolphthalein[2] should always be employed as the indicator in testing anaesthetic chloroforms, since in this case acetic acid is the usual contaminating acid.[4]

(*b*) The amount of $N/100$ potassium hydroxide solution required for neutralization should always be determined. Using 20 cc. of the sample under examination, 10 cc. of water, and 2 drops of phenolphthalein, and titrating as directed above, no more than 0.20 cc. of $N/100$ alkali should be required.

II. THE DECOMPOSITION PRODUCTS OF PURE CHLOROFORM.

(*a*) *The Detection of Carbonyl Chloride.*

Chloroform containing carbonyl chloride gives rise to toxic effects upon administration;[4] and although it is now improbable that accidents can occur from the presence of the oxidation products of pure chloroform, since the necessary precautions are generally exercised in practice to guard against their presence, yet cases have been recorded[5] which show that anaesthetic chloroform which has been carelessly stored for long periods should always be examined for carbonyl chloride as well as the other products of oxidation. When, for any reason, pure chloroform is required for an investigation, it should always be tested for the presence of carbonyl chloride immediately before use.[6]

[1] From these results, Vulpius concluded that the substance giving the acid reaction was more soluble in chloroform than in water, whence the aqueous extract remained neutral to litmus paper. Vulpius did not consider the influence of alcohol, which was undoubtedly present in the samples examined by him, on the dissociation of phenolphthalein alkali.

[2] On the test of Vulpius, see Werner, *Arch. Pharm.*, [3] **25,** 1113.

[3] This, of course, applies generally to the examination of pure chloroform.

[2] Congo red is also very sensitive for this purpose, and may be used when chloroform is being tested qualitatively.

[3] The results obtained on Nos. H, I and J lend strong support to the view of the authors as to the oxidation of anaesthetic chloroform and particularly as to the rôle of alcohol in preservation. None of these samples contained hydrochloric acid or carbonyl chloride.

[4] Carbonyl chloride has an irritating action upon mucous membranes, besides possessing the poisonous properties of carbon monoxide (Dragendorff, *Ermittelung von Giften*, **1895,** p. 62; Kobert-Friedburg, *Practical Toxicology*, **1897,** p. 127). For a full discussion of the toxicological action of carbonyl chloride, see Müller, *Z. angew. Chem.*, **23,** 1489.

[5] For example, Ramsay (*Brit. Assn. Rept.*, **1892**; *J. Soc. Chem. Ind.*, **11,** 772) found that the only impurity in a number of samples of chloroform received from hospitals where death had occurred was carbonyl chloride. It was found to be impossible to look for an unknown impurity in a number of small samples of chloroform; therefore, he exposed a large quantity of "perfectly pure" chloroform to daylight in the presence of air. After "some" months, a considerable quantity of carbonyl chloride was formed, no other product, excepting a trace of hydrochloric acid, having been detected. It was found to be possible to test for carbonyl chloride by pouring a barium hydroxide solution on the surface of a suspected sample, when a white film would appear at the line of division between the chloroform and the water solution. Most of the samples received by Ramsay gave this test, and it was significant that most of the samples were the products of large consignments to hospitals. Ramsay was inclined to believe that the cause of death was the spasmodic contraction of the glottis produced by the carbonyl chloride after the lungs had been thoroughly charged with chloroform. Dott (*Pharm. J.*, [3] **22,** 1080), however, thought that it is in the highest degree improbable that accidents have occurred in the administration of chloroform from the presence of carbonyl chloride. In his opinion, if the amount were considerable, the surgeon would observe the contamination, while if only traces were present, evidence is lacking to show that these would be dangerous. The authors found that samples of anaesthetic chloroform of U. S. P. grade in no case gave a reaction indicative of carbonyl chloride, and even after storage under good conditions for almost two years, such chloroform contained no carbonyl chloride.

[6] For a case in point, see the experiences of Lowry and Magson (*Trans. Chem. Soc.*, **93,** 121), who, in their studies on dynamic isomerism, found that the presence and production of carbonyl chloride in chloroform solutions by the action of air and light would afford a sufficient explanation of all the anomalous results which have been obtained on the arrest of isomeric change in acid chloroform solutions. They found that the active agent in arresting the isomeric change of nitrocamphor dissolved in chloroform is carbonyl chloride.

Carbonyl chloride may often be recognized in samples of decomposed pure chloroform by its peculiar nauseous smell, which is quite different from that of chlorine or hydrochloric acid.[1] If necessary, carbonyl chloride may be detected in the presence of chlorine by agitating the sample of decomposed chloroform with mercury, which combines with the free chlorine, but does not act upon carbonyl chloride, and thus the peculiar odor of this compound becomes more easily recognizable.[2] After the removal of free chlorine by agitation with mercury, moist blue litmus paper is no longer bleached. Prior to the elimination of free chlorine, the reddening of moistened litmus paper may be masked by the action of free chlorine.[3]

Ramsay[4] proposed a test for the direct detection of carbonyl chloride in chloroform which we have found to be satisfactory, providing the proper precautions are observed. This consists in adding clear barium hydroxide solution to the chloroform and allowing the mixture to stand several hours in a stoppered vessel; if carbonyl chloride is present, a white film of barium carbonate forms at the junction of the two liquids.[5] In testing for the presence of carbonyl chloride, whenever a direct test is deemed necessary, the authors operate as follows: To 15 cc. of the sample, contained in a dry glass-stoppered tube of 25 cc. capacity, sufficient of a perfectly clear 1 : 19 barium hydroxide solution is added to fill the tube; after allowing the mixture to stand 3 hours in a dark place, without agitation, the observation as to the formation of a film of barium carbonate is made.

Other direct tests which have been proposed for the detection of carbonyl chloride are the amidophenetol test of Scholvien[6] and the bilirubin test of Pouchet.[7] The barium hydroxide test is, however, entirely satisfactory whenever it is considered necessary to definitely establish the presence of carbonyl chloride; but in general it is sufficient to test the aqueous extract of the chloroform under examination for hydrochloric acid and then make a quantitative determination.[1]

(b) The Detection of Hydrochloric Acid.

Hydrochloric acid and chlorides are not likely contaminants of anaesthetic chloroform at the present time, but pure chloroform should always be examined for their presence. Carbonyl chloride, free chlorine and hydrochloric acid may be recognized in one operation by shaking the sample with silver nitrate solution, which, in the presence of any of these impurities, will produce a white precipitate, whereas pure chloroform gives no reaction with silver nitrate, either in aqueous or alcoholic solution. This is essentially the test generally recommended.[2]

Samples of pure, anaesthetic or commercial chloroform which possess no acid reaction, as determined by titration with $N/100$ potassium hydroxide solution, are assuredly free from carbonyl chloride, chlorine and hydrochloric acid, but pure and anaesthetic chloroforms should also comply with the following test: When 10 cc. of the sample are agitated with 5 cc. of water for 5 minutes, the water extract should not become turbid or give any precipitate upon the addition of silver nitrate solution (absence of hydrochloric acid, chlorides, etc.) and no reduction should occur on warming (absence of acetaldehyde, formic acid and formates, etc.).

(c) The Detection of Chlorine.

It is generally considered that chlorine is a contaminant of anaesthetic chloroform, and accordingly tests are usually specified for its detection. For example, free chlorine and hypochlorous acid are distinguished from hydrochloric acid by their power of bleaching instead of merely reddening litmus, and by liberating

[1] The authors exhibited samples of chloroform which contained carbonyl chloride; these samples fumed in the air and possessed the characteristic odor of carbonyl chloride.

[2] Carbonyl chloride is unaffected by shaking with mercury, but mercury combines with free chlorine (see Martindale's *Extra Pharmacopoeia*, 9th ed., 126).

[3] On these points, see Schacht and Biltz, *Pharm. J.*, **1893,** 1005.

[4] *Loc. cit.* Ramsay also stated that carbonyl chloride may be removed by agitation with slaked lime, but this has been denied (*Brit. Med. J.*, March 16, 1900).

[5] This test is given in the *Nueva Farmacopea Mexicana*, **1904,** 477. In the seventh revision of the *Pharmacopoeia of the United States* (**1893,** 88), the following test was specified: If to about 5 cc. of chloroform contained in a dry test tube of about 10 cc. capacity, about 4 cc. of perfectly clear barium hydrate T. S. be added without agitation, and the test tube be then corked and set aside in a dark place for six hours, no film should be visible at the line of contact of the two liquids.

[6] *Ber. Pharm. Ges.*, **3,** 213. A drop of amidophenetol is dissolved in benzene (anhydrous and free from carbon disulphide) and the suspected chloroform is added to this solution; if carbonyl chloride is present, there is said to be produced an immediate turbidity and later a separation of crystals of diparaphenetol carbamide, insoluble in chloroform. Instead of amidophenetol, Scholvien found that aniline may be used, in which case diphenylcarbamide is formed. In this connection, it may be indicated that Schmidt (*J. prakt. Chem.*, [2] **5,** 35) found that carbonyl chloride reacted with benzamide, giving, among other products, benzonitrile.

[7] *Nouveaux Remedes*, **1904,** No. 13, 289. Pouchet found that if a little of the chloroform under examination is mixed with bilirubin, this dissolves with a green color in the presence of carbonyl chloride and with a brown color in its absence. Merck (*Annual Report*, **18,** 45), however, regarded zinc chloride and starch solution as a more sensitive reagent.

[1] Cf. *Z. anal. Chem.*, **33,** 488. See *Acidity*.

[2] Regnault (*Mon. Sci.*, [3] **12,** 262; *J. pharm. chim.*, [4] **29,** 402) stated that no precipitate should result with silver nitrate; Brown (*Pharm. J.*, [3] **25,** 865) recommended shaking the sample with an equal volume of silver nitrate solution, when no turbidity should be produced; Behal and Francois (*J. pharm. chim.*, [6] **5,** 417) advised that chloroform should neither precipitate nor reduce silver nitrate; White (*Pharm. J.*, [4] **25,** 540) agitates 5 mils of chloroform with 10 mils of water, then tests the water extract; and Krauch (*Testing of Chemical Reagents*, **1902,** p. 77) shakes 2 parts of chloroform with 3 parts of water, and requires that the water extract shall not produce a turbidity on being carefully poured over a solution of silver nitrate in an equal volume of water.

The silver nitrate test has had pharmacopoeial recognition since 1847, when it was required by the *Codex Medicamentarius Hamburgensis* that the water extract should give no precipitate with silver nitrate. The *British Pharmacopoeia* (**1908,** 75) gives the following test for the presence of chlorides: The addition of 4 drops of silver nitrate solution should not produce more than a very slight opalescence in the aqueous portion obtained by shaking chloroform with twice its volume of water for 5 minutes. The *Deutsches Arzneibuch* (**1910,** 118) requires that the water extract of chloroform should not yield any turbidity with test solution of silver nitrate. The silver nitrate test is also given in the pharmacopoeias of Switzerland, Austria, France, Spain, Sweden, Italy, Chili, and Japan. The pharmacopoeias of Switzerland and Austria direct that the chloroform be agitated with an equal volume of water, and that the latter should not then be rendered turbid by silver nitrate solution; the Danish pharmacopoeia requires that the test be made on the aqueous extract obtained by agitating 10 cc. of chloroform with 5 cc. of water; the French *Codex* (**1908,** 148) gives the silver nitrate test for the presence of hydrochloric acid, also stating that no reduction should occur on warming (formates or aldehyde derivatives); the *Pharmacopoea Svecica* (**1908,** 76) specifies that the test be conducted on the water extract, as does the *Farmacopoea Oficial Espanola* (**1905,** 198); and the *Farmacopea Chilena* (**1886,** 147) requires that no precipitation or reduction should occur when the test is applied. The *Pharmacopoeia of Japan* (**1907,** 84) directs that the chloroform be shaken with one-half its volume of water, and that water be carefully poured into a solution of silver nitrate diluted with equal parts of water, when no turbidity should be produced.

iodine from a solution of potassium iodide,[1] zinc iodide[2] or cadmium iodide[3] when the sample or its water extract is shaken with the reagent.

Since free chlorine can only result either through careless purification of chloroform or from the photochemical decomposition of carbonyl chloride, we can now only suspect its presence in pure chloroform which has undergone oxidation. Moreover, it is highly probable that reactions due to hydrogen dioxide have been attributed to free chlorine; and that, especially where potassium iodide was the reagent used, hydrochloric acid and carbonyl chloride were sometimes the cause of the reactions observed. While both pure and anaesthetic chloroform should, of course, give no reaction with potassium or zinc iodide, these reagents lack the reliability required for specific tests, and a 10 per cent. solution of cadmium potassium iodide is considerably more efficient. When this reagent is used, a response is indicative or either the presence of chlorine or hydrogen dioxide, and pure and anaesthetic chloroform should give a negative result in all cases.

12. THE DETECTION OF CHLORINE SUBSTITUTION PRODUCTS.

(a) "Chlorinated Decomposition Products."

The *British Pharmacopoeia* and the *Pharmacopoeia of the United States* give tests for the detection of "odorous decomposition products" and "chlorinated decomposition products" in anaesthetic chloroform.[4]

[1] Potassium iodide is the specified reagent in the pharmacopoeias of Austria, Chili, Denmark, Sweden, Switzerland, and the United States. The Austrian pharmacopoeia requires that no violet color result; the Chili pharmacopoeia that no color result; and the Danish pharmacopoeia that no color be produced on mixing 5 cc. of chloroform with 20 cc. of water and a crystal of potassium iodide. The potassium iodide test is also given in the *Pharmacopoea Croatico-Slavonica* (**1888,** 163), where it is stated that no rose color should result; and in the Finland Pharmacopoeia, where it is required that no violet color result. The *Pharmacopoeia of the United States* (**1905,** 99) specifies that the sample be well shaken with twice its volume of water, and that the water extract be then tested with litmus paper, silver nitrate solution and potassium iodide solution.

[2] The zinc iodide-starch test was recommended by Schwarz and Will (*Pharm. Ztg.*, **1888,** 551); Brown (*Pharm. J.*, [3] **23,** 229) proposed that zinc iodide and starch be used to detect the first signs of decomposition; later Brown (*Ibid.*, [3] **25,** 865) recommended that on shaking with an equal volume of zinc iodide and starch solution, no color should be imparted to the chloroform—a test which he found to be more delicate than that with sirup of iodide of iron and starch; and Krauch (*Testing of Chemical Reagents*, **1902,** 78) states that on shaking with zinc iodide and starch solution, no blue coloration must occur. It has been also considered that the presence of free chlorine is sufficiently indicated by the coloration of moistened test paper charged with zinc iodide and starch when it is immersed in the atmosphere of the container.

The *Deutsches Arzneibuch* (**1910,** 118) states that when the water extract of chloroform is shaken with zinc iodide and starch solution, the latter should not become blue or colored. The *Pharmacopoeia of Japan* (**1907,** 84) requires that chloroform acquire no coloration on shaking with a solution of zinc iodide and starch, and that the latter acquire no blue coloration.

[3] The *British Pharmacopoeia* (**1908,** 75) directs that the aqueous portion obtained by shaking chloroform with twice its volume of water for 5 minutes should not afford any color with 1 cc. of cadmium iodide T. S. and 2 drops of mucilage of starch. The same reagents are required in Belgium.

[4] The *British Pharmacopoeia* requires that 2 cc. of the sulphuric acid liquid, obtained on shaking chloroform with 1/10 its volume of sulphuric acid for 20 minutes, and then set aside for 15 minutes, when diluted with $2^1/_2$ times its volume of water, should remain clear, almost colorless, and should possess a pleasant odor; that the liquid should still retain its transparency and freedom from color, even when further diluted with 10 cc. of water and stirred with a glass rod, and the transparency should not be more than slightly diminished on the addition of 4 drops of silver nitrate solution; and that the addition of silver nitrate solution should not more than slightly diminish the transparency of the aqueous portion obtained by shaking the sulphuric acid—treated chloroform with twice its volume of water. The *Pharmacopoeia of the United States* gives a similar test. See Section 3(*a*).—*The Test with Sulphuric Acid.*

Anaesthetic chloroform which has been properly purified and stored should comply with these requirements,[1] although there are on record instances[2] which show that officinal chloroform of the present pharmacopoeial grade occasionally contains "chlorinated decomposition products," probably resulting from the careless storage, especially for protracted periods of time, of insufficiently pure products.

The phrase "chlorinated decomposition products" is indefinite and rather vague, but it includes a class of compounds, resulting either from manufacture ("chlorinated oils," previously referred to; chlorine substitution products decomposable by sulphuric acid; etc.), in which case such contamination is only likely when the chloroform has not been purified by a process serving for their elimination; or from the oxidation of anaesthetic chloroform (chlorinated derivatives of the oxidation products of alcohol, chlorocarbonic ether, etc.). In the latter case, the formation of such compounds can only result after the oxidation of the alcohol has reached a maximum, and consequently their occurrence is only likely in samples which have been stored for long periods of time under conditions conducive to oxidation.

(b) The Occurrence of Ethyl Chloride in Chloroform.

Until 1904, it was generally assumed that commercial chloroform prepared from acetone was identical with that made from alcohol, although the clinical experiences of some English anaesthetists indicated that the anaesthetic chloroform prepared therefrom is distinctly inferior to the product from alcohol. For example, it was observed that the patient often had an undue tendency to cough and hold the breath, and the prolongation of the time of induction thus effected increased the danger of an overdose. In 1904, Wade and Finnemore[3] published the results of their investigation as to the existence of a volatile impurity in chloroform prepared from alcohol. They found that the presence of a minute quantity of ethyl chloride in chloroform made from alcohol, probably about 0.05 per cent. (about 2 cc. per Winchester quart), would account for its physical behavior; and they stated that they had substantiated by clinical experience the conclusion that the volatile substance which "improves" the anaesthetic properties of chloroform made from alcohol, but is absent from chloroform made from acetone, is ethyl chloride. According to Wade and Finnemore, "acetone chloroform" to which a small quantity of ethyl chloride had been added was therapeutically identical with chloroform made from alcohol.[4]

[1] The authors have experimentally demonstrated that this is the case.

[2] For example, Ohliger (*Proc. Mich. Pharm. Assn.*, **1906,** 47) reported chloroform with "chlorinated compounds" and "carbonizable impurities" present; and Caspari (*Proc. Mo. Pharm. Assn.*, **1906,** 100) examined seven samples of chloroform, out of which two contained "chlorinated decomposition products."

[3] *J. Chem. Soc.*, **85,** 938.

[4] It has therefore been proposed to add a minute of ethyl chloride to chloroform made from acetone (*Schweiz. Wochschr.*, **47,** 302). It has been stated that the addition of 0.25 per cent. of ethyl chloride to chloroform prepared from acetone renders it physiologically identical with the product from alcohol (*Trans. Soc. Anaesth.*, **7,** 89). In fact, there has been

Dott[1] confirmed the observation that a small proportion of ethyl chloride is formed in preparing chloroform from ethyl alcohol. He found that, unlike most impurities, it is not removed by washing with water,[2] treatment with sulphuric acid, or with soda solution.

While ethyl chloride, when present in small proportions in anaesthetic chloroform, is not, strictly speaking, an objectionable impurity, and although it may, according to some, prevent a prolongation of the period of induction, yet anaesthetic chloroform manufactured from acetone in this country has been found by American anaesthetists to be fully as satisfactory as that from other sources, and this may be said to be general when the chloroform is properly made from purified acetone and the product is carefully purified. When chloroform is prepared from alcohol, ethyl chloride may be easily formed in the course of chlorination, while it is difficult to conceive how it could be formed from acetone under these conditions; but ethyl chloride comes over with the first distillate on rectifying. The anaesthetist should know the preparation he is using, and if he desires chloroform containing ethyl chloride he should specify "chloraethoform" or a similar preparation. Anaesthetic chloroform should, without exception, be free from contamination with ethyl chloride, for each compound exerts its specific physiological action.

Since the boiling point of anaesthetic chloroform may be lowered 2° C. by the presence of 0.1 per cent. of ethyl chloride, this impurity may be detected by fractionation.

(c) *The Occurrence of Ethylene Chloride in Chloroform.*

Ethylene chloride has, in the past, been regarded as a contaminant of chloroform, and several tests have been proposed for its detection[3]; but its presence in anaesthetic chloroform is not to be expected now.[4] The isomer, ethylidene chloride, is, however, a probable contaminant of chloroform prepared from alcohol,[5] since it is more difficult to eliminate by rectification; and even though it is said to possess anaesthetic properties similar to those of chloroform, its presence should be known for the reasons indicated in the case of ethyl chloride.[1]

(d) *The Detection of Carbon Tetrachloride.*

Chloroform is now being manufactured from carbon tetrachloride; therefore the detection of this likely contaminant should be considered, although we have so far been unable to find a chemical method which is suitable for the recognition of probable amounts in anaesthetic chloroform.[2] The method given in the French *Codex*[3] is unsatisfactory, and the manufacturers of chloroform from carbon tetrachloride state that they are aware of no method of determining the presence of carbon tetrachloride in chloroform except by the specific gravity—that is, by taking some chloroform which is known to be pure and diluting it with various percentages of pure carbon tetrachloride, they have found that a scale may be made which is of sufficient accuracy for the purpose. It is true that mixtures of pure chloroform and pure carbon tetrachloride may be determined in this way, and the method is undoubtedly suitable for factory control, yet it is highly desirable that a method be found which is applicable in the presence of the variables of anaesthetic chloroform and is of sufficient delicacy for the detection of small amounts. Since it has been stated that all chloroform contains traces of dichlormethane,[4] the detection of this compound is likewise of importance.[5]

Since the variables of anaesthetic chloroform of the present pharmacopoeial grade also render the determination of small amounts of carbon tetrachloride by means of the boiling point[6] and conductivity methods, and by an estimation of total chlorine, inapplicable, an investigation was made to ascertain whether carbon

placed on the market a preparation of chloroform containing 0.25 per cent. of ethyl chloride, called "chloraethoform" (*Chem. and Drug.*, **1904,** 1289).

[1] *J. Soc. Chem. Ind.*, **27,** 272.

[2] In 1875, Normandy-Noad (*Commercial Chemical Analysis*, p. 122) stated that "hydrochloric ether" may be recognized in chloroform by shaking the latter with water, then decanting the aqueous extract and distilling it from a water-bath. They mention that the odor of the ether is very evident in the portions which first come over.

Others state that the presence of ethyl chloride may be recognized by distilling the chloroform with water on a water bath, when the first portions of the distillate will possess a distinct odor of the foreign body.

[3] Hager (*Kommentar*, **1865,** 443) stated that the test with sodium serves for the detection of alcohol and ethylene chloride; he also reported that ethylene chloride may be detected by means of potassium hydroxide, ethylene being evolved. It has been proposed that ethylene chloride be detected in chloroform by drying the sample by agitation with dry potassium carbonate, and then adding potassium, which produces chlor-ethylene, a gas possessing an alliaceous odor, in the presence of the impurity.

On the boiling points of mixtures of ethylene chloride and chloroform, see Wulf, *Inaugural Dissert.*, Berlin, June 26, 1885.

Keppeler (*Anaesthetica, Loc. cit.*), in one of the 101 fatal cases of chloroform administration collected by him, states that allyl chloride was found in the chloroform, although the same chloroform had been used without bad effects in other cases.

[4] Any ethylene chloride present in the crude product is removed by means of the rectification processes now in use.

[5] See Krämer, *Ber.*, **3,** 257, and Regnault, *Ann. chim. phys.*, [2] **71,** 355.

[1] Allen (*Commercial Organic Analysis*, **1,** 235) considered it very doubtful whether the substance in chloroform of the formula $C_2H_4Cl_2$ is always ethylene chloride, but that it is probably more frequently the isomer $CH_3.CHCl_2$.

Ethylidene chloride possesses an odor and taste similar to those of chloroform, a boiling point of 58–60°, and is difficult to detect when present in chloroform in small amounts. On its conduct with sodium, potassium, and potassium hydroxide, see Tollens, *Ann.*, **137,** 311.

[2] The investigation is being continued in this laboratory.

[3] **1908,** 148. The method given is as follows: Agitate 1 part of chloroform with 100 parts of water previously saturated with carbon tetrachloride, and finally with 20 parts of this same water; the carbon tetrachloride, if it is present in sensible proportions, will remain undissolved, while the chloroform dissolves completely.

This test is evidently based upon the one proposed by Robineau and Rollin (*Mon. Sci.*, [4] **1,** 341), who found that when 400 cc. of water, previously saturated with carbon tetrachloride, are shaken with 1 cc. of the chloroform in question, the liquid will become turbid even in the presence of 0.1 per cent. of carbon tetrachloride. The same authors mention another test which is of no value. 1 cc. of the chloroform to be tested is put in a sealed tube with 10 cc. of sodium carbonate (36° Bé.) and 10 cc. of water, and the mixture is heated for 7–8 hours at 100° C. Sodium carbonate does not attack carbon tetrachloride, consequently the appearance of oily drops shows the presence of this compound.

The test mentioned by Margosches ("Der Tetrachlorkohlenstoff," p. 78) for distinguishing chloroform from carbon tetrachloride—that based on the fact that chloroform is immediately intensely colored by the addition of wood-tar pitch, whereas no coloration results in the case of carbon tetrachloride—is not suitable for proving the presence of carbon tetrachloride in chloroform.

[4] See Section VI, 6.

[5] The physiological action of dichlormethane requires investigation.

[6] In this connection it should be mentioned that Haywood (*J. Phys. Chem.*, **3,** 318) found that chloroform, otherwise pure, containing 7.8 per cent. of carbon tetrachloride, boils at 62° at 758.1 mm.

tetrachloride might be determined in anaesthetic chloroform by reduction, or rather by a method based upon the probably different degrees of reducibility of carbon tetrachloride and chloroform, and then determining the hydrochloric acid formed. For this purpose, zinc and sulphuric acid[1] and copper-zinc couple[2] are unsuitable; accordingly finely-divided iron was first tried as the reducing agent, since it has been stated that the reduction of carbon tetrachloride by means of this agent may be readily controlled, so that little or no reduction to dichlormethane occurs.[3]

In the experiments with reduced iron, varying amounts (0.5–10 g.) of the latter were added to mixtures of water (10–50 cc.) and anaesthetic chloroform (20–150 cc.) containing known amounts of carbon tetrachloride, both with and without the addition of small amounts of sulphuric acid, and the reaction was studied at various temperatures during different periods of time. In every experiment a blank anaesthetic chloroform free from carbon tetrachloride was run under the same conditions. In these experiments it was invariably found that chloroform also underwent reduction, as shown by the formation of hydrochloric acid, and it is concluded that the presence of likely amounts of carbon tetrachloride in anaesthetic chloroform cannot be recognized with accuracy by such a method. Palladium hydride gave similar results.

It should be mentioned here that carbon disulphide—a possible contaminant of commercial chloroform prepared from commercial carbon tetrachloride—may be recognized in chloroform by means of the method of Schmitz-Dumont[4] for the detection of this compound in carbon tetrachloride.

13. SCHEME FOR THE EXAMINATION OF CHLOROFORM FOR ANAESTHETIC AND ANALYTICAL PURPOSES, WITH PARTICULAR REFERENCE TO THE DETECTION OF AVOIDABLE IMPURITIES.

1. Specific Gravity. The specific gravity should be determined by means of a pycnometer at 15° C. (see discussion under *Specific Gravity* and *Alcohol*).

2. Odor. In the case of *anaesthetic chloroform*, 100 cc. of the sample are slowly evaporated over a water-bath until about 10 cc. remain in the flask. This residuum should be colorless and should possess no foreign odor, and when it is allowed to evaporate on filter paper, at room temperature, there should result no odor of fusel oil, empyreumatic matter, or other substances than *chloroform* and *ethyl alcohol*, as the last portions disappear. If a decided odor is imparted to the filter paper after the evaporation of the residue, or if any foreign odor is observed during the course of evaporation, the chloroform should be rejected, but for further information, may be tested for such impurities as fusel oil, chlorinated derivatives of alcohol, acetone, or the higher alcohols, extractive matter, etc.

Pure chloroform should also comply with this requirement, except that as the last portions of the residuum evaporate on filter paper, no odor of other substances than *chloroform* should be apparent.

3. Residue. When 100 cc. of either *pure* or *anaesthetic* chloroform are allowed to evaporate in a platinum dish at 100° C., there should be left no weighable residue. In every case this should be determined gravimetrically and not by vision.

4. Organic Impurities. When 20 cc. of *anaesthetic chloroform* are mixed with 15 cc. of concentrated sulphuric acid in a glass-stoppered tube of 50 cc. capacity which has been previously rinsed with concentrated sulphuric acid, no visible coloration should be imparted to the mixture after the addition of 0.4 cc. of pure 40 per cent. formaldehyde solution, and then shaking throughout a period of five minutes.

Pure chloroform should, of course, also comply with this test; in fact, in this case, no coloration should result even after one hour, providing the mixture is allowed to stand in the dark.

5. Water. *Pure chloroform* and *anhydrous anaesthetic chloroform* should comply with the following test: When 20 cc. of the sample are boiled over one gram of clean crystals of calcium carbide, and the vapors evolved are passed into ammoniacal silver nitrate solution, no acetylene reaction should result.

Anaesthetic chloroform should readily conform to this test: When 10 cc. of the sample are agitated with an equal volume of paraffin oil (sp. gr. 0.880), the oil should dissolve to a clear solution without any evidence of a turbidity.

6. Alcohol. *Pure chloroform* should possess a correct specific gravity and should comply with the following: 10 cc. are shaken in a separatory funnel with 4 cc. of concentrated sulphuric acid; the extraction is again repeated with 4 cc. of sulphuric acid, and finally with 2 cc. The sulphuric acid solution is now mixed with 40 cc. of water, and the diluted solution is gently distilled until the distillate amounts to about 20 cc. To 10 cc. of the distillate, 6 drops of a 10 per cent. solution of potassium hydroxide are added and the liquid is warmed to about 50° C. A solution of potassium iodide fully saturated with free iodine is next added, drop by drop, with agitation, until the liquid becomes permanently yellowish brown in color, when it is carefully decolorized with potassium hydroxide solution. No iodoform should be deposited at the bottom of the tube. This test is not peculiar to alcohol, being produced also by acetaldehyde, propyl alcohol, acetone, etc.; but *pure chloroform* should give an absolute non-response. As confirmatory tests, apply tests 1(*a*), 1(*b*) and 3(*b*) of Section 5.

In the case of *anaesthetic chloroform* and *commercial chloroform*, an indication as to the amount of alcohol present may be had from the density of the sample as determined in 1; but no definite conclusions should be arrived at until a quantitative estimation of the alcohol has been made by the method of Nicloux as elaborated by the authors [see 1(*a*), Section 5] or as modified by Behal and François.

[1] These reagents convert chloroform into dichlormethane (Geuther, *Ann.*, **107**, 212; Richardson, *Chem. News*, **18**, 60).

[2] Owing to the presence of water and alcohol in anaesthetic chloroform (Gladstone and Tribe, *J. Chem. Soc.*, **28**, 508).

[3] Smith, U. S. Patent 753,325, March 1, 1904.

[4] *Chem. Ztg.*, **21**, 487, 510. When this test is applied to chloroform, it is necessary to run a blank test on *pure* anaesthetic chloroform, for metallic silver is precipitated in all cases by reduction, and consequently this precipitate must be distinguished from silver sulphide. Generally, if the precipitate possesses no black color, it may be assumed that no carbon disulphide is present. This method is the best available for the purpose.

Inghilleri (*Gazz. chim. ital.*, **39**, I, 634) found that carbon disulphide and ammonium carbonate form ammonium thiocyanate quantitatively when heated for four hours in alcohol at ordinary pressure. We found, however, that this method does not serve for the detection of such traces of carbon disulphide as are likely to occur in commercial chloroform prepared from carbon tetrachloride. When carbon disulphide is added to anaesthetic chloroform, and the method of Inghilleri is applied, the former does not undergo quantitative conversion into ammonium thiocyanate, and, in addition to the latter, we have found that ammonium thiocarbamate is formed, especially when a considerable amount of alcohol is present.

7. Acetone.

Pure chloroform complying with the iodoform test (6, *supra*) is assuredly free from acetone.

Anaesthetic chloroform should give a negative reaction in all cases when the following exclusion test is applied: 10 cc. of the sample are agitated with 5 drops of a 0.5 per cent. sodium nitroprusside solution and 2 cc. of ammonium hydroxide (sp. gr. 0.925), and the mixture is then allowed to stand for several minutes. Chloroform containing up to 1 per cent. of alcohol may impart a yellowish brown color to the supernatant liquid on agitation, but when acetone is present an amethystine color results. This test must be conducted in the cold. After application to the suspected chloroform direct, the first 10 per cent. distillate and the 10 per cent. residuum, obtained by allowing 100 cc. of the sample to slowly distil, should be tested. When the proportion of acetone to chloroform is 1 : 500, the amethyst color is marked; but in the presence of 1 part in 1000, the coloration is not distinct until the mixture of chloroform with ammonium hydroxide and sodium nitroprusside has been saturated with ammonium sulphate, shaken and then allowed to rest for five minutes. It is advisable, in all cases, to run a blank test on *pure* anaesthetic chloroform for comparison. Since acetaldehyde is generally present in fresh and properly stored samples of anaesthetic chloroform in proportions greater than 1 : 3300, usually the reaction is not interfered with by this substance, but in every case the sample should be examined for the presence of acetaldehyde, and if it complies with test 8(*a*), a positive reaction upon applying the acetone test may be said to be solely indicative of the presence of acetone.

8. Acetaldehyde.

(*a*) *Chloroform of all grades* should pass this exclusion test: 5 cc. of the sample are agitated with 5 cc. of the reagent of François (see Section 9A) in a glass-stoppered tube; no coloration should result even after 15 minutes. The presence of 3 parts of acetaldehyde by volume in 10,000 of chloroform may thus be made evident and smaller amounts may, of course, be detected by resorting to fractionation.

(*b*) *Pure chloroform* giving a negative reaction on the application of test 6 may be regarded as free from acetaldehyde; but it should, in addition, give no response when 5 cc. are agitated with 5 cc. of Nessler's reagent, U. S. P., and the mixture is allowed to stand 5 minutes.

When 10 cc. of *anaesthetic chloroform* are agitated with 10 cc. of water and 5 drops of Nessler's reagent, U. S. P., and the mixture is then allowed to stand for 5 minutes, there should result no precipitate, and the reagent should assume *no coloration*, although it may become opalescent or slightly turbid.

9. Acidity.

When 20 cc. of either *pure or anaesthetic chloroform* are thoroughly agitated with 10 cc. of water and 2 drops of phenolphthalein solution and then titrated with *N*/100 potassium hydroxide solution, added drop by drop, not more than 0.2 cc. of standard alkali solution should be required to produce a faint but decided alkaline reaction permanent for 15 minutes, when the mixture is shaken 30 seconds after the addition of each drop of alkali. If the presence of free acid is indicated, the sample should be rejected, but for further information may be examined for the oxidation products of pure chloroform and alcohol.

10. The Decomposition Products of Pure Chloroform.

(*a*) *Carbonyl chloride.* To 15 cc. of the sample, contained in a dry glass-stoppered tube of 25 cc. capacity, sufficient of a perfectly clear 1 : 19 barium hydroxide solution is added to fill the tube; after allowing the mixture to stand three hours in a dark place without agitation, the observation as to the formation of a film of barium carbonate is made.

(*b*) *Hydrochloric acid and Chlorides.* Samples of chloroform complying with 9 are assuredly free from carbonyl chloride, hydrochloric acid and chlorine; but pure and anaesthetic chloroforms should also conform to the following test: When 10 cc. of the sample are agitated with 5 cc. of water for 5 minutes, the water extract should not become turbid or give any precipitate upon the addition of silver nitrate solution (absence of hydrochloric acid, chlorides, etc.), and no reduction should occur on warming (absence of acetaldehyde, formic acid and formates, etc.).

(*c*) *Chlorine* (*and Hydrogen dioxide*). When 10 cc. of the sample are agitated during 15 minutes with 10 cc. of a 10 per cent. cadmium potassium iodide solution, there should result no liberation of iodine as determined by the addition of starch solution. *Chloroform of all grades should give a negative reaction with this test.*

11. The Decomposition Products of Anaesthetic Chloroform.

(*a*) The detection of *acetaldehyde* has already been referred to (8).

(*b*) *Anaesthetic chloroform* failing to comply with test 9, and which contains none of the substances referred to in 10 (this will generally be found to be the case), should be rejected, since then the indication is that *acetic acid* is present.

(*c*) When 20 cc. of *anaesthetic chloroform* are shaken during 20 minutes with 15 cc. of concentrated sulphuric acid in a glass-stoppered tube of 50 cc. capacity previously rinsed with sulphuric acid, and 2 cc. are diluted with 5 cc. of water, the liquid should remain colorless and clear, and should possess no odor foreign to anaesthetic chloroform (chloroform and alcohol); and the liquid should retain its transparency and colorless state when further diluted with 10 cc. of water, and the transparency should not be diminished on the addition of 5 drops of silver nitrate solution. A positive result is indicative of the presence of chlorinated derivatives of the oxidation products of alcohol, etc. [see Section 12(*a*)].

14. THE DEGREES OF PURITY OF AMERICAN CHLOROFORMS.

The main impurities contained in American anaesthetic chloroforms are, besides water, impurities decomposable by sulphuric acid and traces of the oxidation products of ethyl alcohol. As previously mentioned, the presence of small amounts of ethyl alcohol is necessary; but anaesthetic chloroform should contain but mere traces of water, and it is desirable that it be absolutely water-free. The necessary precautions should be taken by manufacturers to guard against the presence of organic impurities as well as of extractive matter—a common contaminant of anaesthetic chloroform contained in unprotected cork stoppered bottles.

The following table will serve to show the comparative purity of various samples of chloroform. Nos. 1–9 were samples of anaesthetic chloroform, supposed to be of the present U. S. P. grade and such as are now being supplied to the trade;[1] No. 10 was a sample, stated to be of U. S. P. quality, contained in a tin and 17 months old; No. 11 was a sample of "Chloroform for Anaesthesia," contained in a sealed tin, and 6 years old;[2] and No. 12 was an unopened tin

[1] All of these samples, with the exception of No. 6, were manufactured in the United States. These samples were obtained through the courtesy of the various manufacturers, to whom the authors desire to acknowledge their indebtedness.

[2] This sample was kindly supplied by Surgeon-General Torney, U. S. A. It was dated November 1, 1905.

COMPARATIVE PURITY OF VARIOUS SAMPLES OF CHLOROFORM.

All samples gave tests for water present in permissible amounts; negative acidity tests U. S. P., negative tests for chlorides and for oxidation products of pure chloroform

No.	Source	Grade	Density at 25°/25°.	Odor	Residue in g. per liter
1	Acetone	Anaesthetic	1.4827	Normal	
2	Acetone	Anaesthetic	1.4730	Normal	None
3		Anaesthetic	1.4772	Normal	None
4	Acetone	Anaesthetic	1.4806	Normal	None
5	Acetone	Anaesthetic	1.4770	Normal	
6	Chloral Acetone	Anaesthetic	1.4839 1.4756	Normal Normal	
8	Acetone	Anaesthetic	1.4750	Normal	
9	Carbon tetrachloride	Anaesthetic	1.4773	Normal	
10		Anaesthetic	1.4751	Slightly pungent	0.0220
11	Acetone	Anaesthetic	1.4722	Normal	None
12	Alcohol	Anaesthetic	1.4747	Fruity	
13	Acetone	Analytical	1.4752	Normal	0.0165
14	Acetone	Commercial	1.4846	Normal	0.0705

No.	Extractive matter.	Sulphuric acid test	Formalin sulphuric acid test	Absolute ethyl alcohol in cc. per 100 cc.	Higher alcohols.
1	Present from cork.	Faint	Faint brown	0.50	Not detected
2	Absent	Negative	Faint yellow	0.97	Not detected
3	Absent	Negative	Marked brown	0.77	Not detected
4	Absent	Negative	Negative	0.56	Not detected
5	Absent	Negative	Brown color	0.70	Not detected
6	Present from luting	Marked		0.30	Not detected
7	Present from cork.	Decided		0.80	Not detected
8	Indefinite	Faint	Very faint yellow	0.84	Not detected
9	Trace	Very faint	Faint yellow	0.74	Not detected
10	Trace	Faint		0.84	Not detected
11	Absent	Marked		0.83	Present
12	Present	Pronounced		0.60	Propyl
13	Present from cork.	Faint		0.69	Not detected
14	Present	Marked			Not detected

No.	Acetone.	Acetaldehyde.	Acetic acid in g. per 100 cc.	"Odorous decomposition products."	"Chlorinated decomposition products."
1	Absent		0.0003	Absent	Absent
2	Absent	Trace	0.0001	Absent	Absent
3		Trace		Absent	Absent
4	Not detected.	Trace	Absent	Absent	Absent
5	Not detected.		Absent	Absent	Absent
6		Trace	0.00015	Faint reaction	Trace
7	Not detected.	Trace	0.00015	Absent	Very faint reaction
8	Not detected.	Trace	0.00030	Absent	Present
9		Absent	Absent	Absent	Absent
10		Present	0.00045	Absent	Present
11	Not detected.	About 1 : 3300	0.0009	Absent	Present
12		1 : 2000	0.00045	Present	Absent
13	Not detected.	Trace		Absent	Faint reaction
14	Not detected.	Trace		Absent	Faint reaction

of "Chloroformum Purificatum," manufactured in 1863 or shortly before.[1] The last two samples are of particular interest, since, so far as the authors are aware, they were the oldest samples of chloroform ever examined.

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[1] This sample was also furnished by Surgeon General Torney, U. S. A., who stated that the chloroform was taken out of a pannier of the variety issued during the Civil War, along with records, etc., which bore the date of 1863. To quote from his letter of transmittal: "I presume that the chloroform was made at that period, or before, and I may say that it is the last survivor, so far as I know, of the chloroform supplied at that period." It is important to note that this tin of chloroform possessed a smaller air space than No. 11, the container being almost full; this, no doubt, accounts for the difference in oxidation of the alcohol in the two samples.

ON THE STARCH OF GLUTINOUS RICE AND ITS HYDROLYSIS BY DIASTASE.

By YOSHIO TANAKA.

Received February 12, 1912.

While it is well known that starch granules or their solutions are colored intensely blue by a dilute solution of iodine, there is another variety of starch which gives a pure red coloration with the same reagent. Kreusler[1] discovered the presence of such starch in glutinous rice. This variety of starch seems to be quite widely distributed in plants. The writer has found that the starches of "mochi-awa" (glutinous millet), "mochi-kibi" (glutinous variety of Panicum miliaceum L.), "morokoshi" (Andropogon Sorghum Brot. var. vulgaris Hack.) and "nien kaoling" (glutinous variety of "kaoliang") are also colored red by iodine solution.

The peculiar nature of the starch of glutinous rice has been investigated by several authors. Kreusler thought that the red coloration of the starch in glutinous rice, produced by iodine, might be due either to some substance which hindered the ordinary blue coloration of starch, or to some special modification of starch. F. W. Dafert[2] considered that the starch of glutinous rice contains erythroglanulose—the main part of which consisted of erythrodextrin. R. W. Atkinson[3] held that the red coloration was more probably due to special albuminoids than to dextrin. J. Shimoyama[4] attributed this reaction to the presence of a large quantity of Nageli's amylodextrin.

Notwithstanding all these investigations the nature of the starch of glutinous rice is not yet clearly explained and, therefore, research to ascertain the constituents of the starch is not only interesting but necessary from both scientific and practical points of view.

Glutinous rice (Japanese mochi-gome)—Oryza glutinosa—has long been widely used in Japan such as in preparing "Mochi" (a kind of cake prepared by kneading steamed glutinous rice), "Ame" (a sweet prepared by saccharification of cooked glutinous rice by means of malt), "Mirin" (a liquor which is prepared from steamed glutinous rice, koji and spirit), etc.

Since the glutinous rice obtained in the market generally contains common rice, the latter must be removed when the glutinous rice starch is to be used for investigation. The author prepared the starch according to the ordinary process, from glutinous rice, from which common rice had been carefully removed. The separation of common rice from glutinous rice can easily be effected as the former is translucent while the latter is opaque.

The glutinous rice starch forms a white, tasteless and odorless powder; examined under the microscope the granules are almost identical in shape and size with those of the starch obtained from common rice.

BEHAVIOR OF GLUTINOUS-RICE-STARCH WITH IODINE.

A fine red coloration of glutinous-rice-starch with

[1] U. Kreusler, *Jahres-Bericht chem.-tech.*, **1885,** 657.

[2] F. W. Dafert, *Ibid.*, **1886,** 610.

[3] R. W. Atkinson, *Chem. Sake Brew.*, **1882,** 2.

[4] J. Shimoyama, *J. Shimoyama's Pharm. Chem.*

iodine is observable only after the structure of the starch cell has been destroyed, either by heat or mechanical means. The color produced by iodine with intact grains is a dirty reddish brown. It is, therefore, true that the inner contents of the starch cell alone are colored pure red by iodine, just as the granulose of common starch is colored blue by iodine.

The author made comparative tests on ungelatinized starches obtained from different sources as to their color reactions toward iodine in presence of water. Three grams of each starch were shaken up with 100 cc. of $N/20000$ and $N/1000$ iodine solutions respectively. After ten minutes the color reactions were observed as follows:

Ungelatinized starch from:	Reaction with N/20000 iodine solution.	Reaction with N/1000 iodine solution.
Glutinous rice	Light red	Reddish brown
Common rice	Light red	Purplish blue
Potato	Light purplish red	Blue
Sweet potato	Light purplish red	Blue

The author then tried to ascertain whether or not glutinous rice starch contains common starch.

It is known that common starch possesses greater affinity for iodine than erythrodextrins, therefore, a minute quantity of the former can be detected to a certain extent even in the presence of a larger amount of the latter if a weak iodine solution is carefully added, drop by drop. Again, common starch possesses also greater affinity for iodine than glutinous rice starch, and therefore, the above method may also be applied in order to detect the presence of a small quantity of common starch in glutinous rice starch. Experiments based on the above method led the author to think that glutinous rice starch does not contain common starch, since no blue coloration could be observed with the gelatinized solution of the starch.

The author observed very interesting facts about the coloration of both common starch and the starch of glutinous rice. When glutinous rice starch is suspended in $N/100$ iodine solution without gelatinization and then sodium sulphate is added to saturation, the red coloration which first appeared discolored to a dark tint with a bluish shade. When the blue starch-iodide obtained with potato starch is treated with carbon bisulphide, chloroform or a careful proportion of sodium thiosulphate, the blue coloration turned into a violet or reddish tint. These facts suggest the probability that what is generally known as starch-iodide is not at all a definite chemical compound but a solid solution of iodine in starch. The intensity and shade of color relates to the degree of quantity of iodine therein dissolved, the larger the quantity dissolved the more bluish it appears, while in the least quantity it will appear red. The solubilities of iodine in various starches may be dependent upon the nature of the starch. This view, I believe, can be confirmed by the fact that the blue colored starch iodide is changed into a red compound when it is washed with a potassium iodide solution or with alcohol.

ABSENCE OF ERYTHRODEXTRIN AND ACHROODEXTRIN IN THE STARCH.

It is well known that the consistency of common rice starch paste, gelatinized by means of heat or caustic alkalis, is slightly thinner than that of potato starch. Arthur Meyer explained this peculiarity by an assumption that common rice starch contains more or less soluble starch, but such is somewhat doubtful. The fact that the consistency of glutinous rice starch paste is equal to that of common rice starch, leads to the assumption that the essential constituents of glutinous rice starch are not dextrins; because if, other things remaining the same, glutinous rice starch contains a large amount of dextrins the consistency of its gelatinous paste ought to be thinner than that of the common rice starch paste. It can, therefore, be deduced that, even if dextrins are contained in glutinous rice starch, the quantity is not considerable. The author intended to show the absence of erythrodextrin and achroödextrin in the starch, taking advantage of the behavior of glutinous rice starch toward baryta water.

Bülow discovered that the so-called Lintner and Dull's amylodextrin and erythrodextrin are both precipitated by baryta water, while achroödextrin is precipitated only in an alcoholic medium. The limits of precipitation of several dextrins by baryta water were investigated by D. Moreau.

In accordance with Moreau's[1] method the author also determined the minimum quantities of baryta water with which all kinds of dextrins as well as starch paste are precipitated. For such testing 2 cc. each of a 1 per cent. solution of the samples were taken in test tubes with cork stoppers into which a measured amount of water and saturated baryta water (sp. gr. 1.027) was added and shaken, the volume of the mixture in each test tube being made 10 cc. After standing for 24 hours the clear supernatant solution was filtered and the filtrate examined by an iodine solution after acidifying with acetic acid. The results obtained were as in the following table:

Starch or dextrin solution, cc.	Water, cc.	Baryta water, cc.	Iodine reaction of acidified filtrates: Potato starch.	Common rice starch.	Glutinous rice starch.	Soluble potato starch.	Soluble glutinous rice starch.	Erythrodextrin
2	7.6	0.4	.....	.....	..	.....	..	...
2	7.4	0.6	blue	blue	red	.....	..	...
2	7.2	0.8	light blue	blue	red	blue	..	...
2	7.0	1.0	none	slightly blue	red	blue	red	...
2	6.8	1.2	none	none	pink	blue	red	...
2	6.6	1.4	none	none	none	reddish blue	red	red
2	6.4	1.6	none	none	none	reddish blue	red	red
2	6.2	1.8	none	none	none	light bluish violet	red	red
2	6.0	2.0	none	none	none	light violet	pink	red
2	5.8	2.2	none	none	none	light violet	pink	red
2	5.6	2.4	none	none	none	faint pink	pink	red
2	5.4	2.6	none	none	none	faint pink	light pink	red
2	5.0	3.0	none	none	none	none	none	red
2	4.0	4.0	none	none	none	none	none	pink
2	3.0	5.0	none	none	none	none	none	pink
2	2.0	6.0	none	none	none	none	none	pink

[1] D. Moreau, *Wochenschrift für Brauerei*, **1905**, No. 344.

From these results the minimum quantity of the baryta solution, which precipitates dextrins or starches respectively after 24 hours, is calculated as follows:

Starch or dextrin	Baryta solution
Potato starch	1.0 cc.
Common rice starch	1.2 cc.
Glutinous rice starch	1.4 cc.
Soluble potato starch (Lintner's)	2.4 cc.
Soluble glutinous rice starch (Lintner's)	3.0 cc.
Erythrodextrin	above 6.0 cc.

Thus it will be seen that the glutinous rice starch closely resembles common starch as regards its behavior toward baryta water, while the soluble-glutinous-rice-starch, which was prepared by Lintner's method and which is colored red by iodine, resembles the soluble potato starch rather than the erythrodextrin.

In studying the effect of soluble starch or erythrodextrin upon the quantity of baryta water when one of either is added in small quantity respective samples of starches in question, it was expected that the minimum quantity of baryta water to be used would be greater than that starch sample alone would require. The accuracy of this expectation is to be found in the results obtained and tabularly arranged as follows:

Carbohydrate solution.	Solution taken cc.	Minimum quantity of baryta water to precipitate the carbohydrate, cc.
1 per cent. potato starch solution, 100 cc.	2.0	1.6
1 per cent. soluble starch solution, 1.0 cc.	...	...
1 per cent. glutinous rice starch solution, 100 cc.	2.0	1.6
1 per cent. erythrodextrin solution, 1.0 cc.	...	...
1 per cent. glutinous rice starch solution, 100 cc.	2.0	1.8
1 per cent. erythrodextrin solution, 2.0 cc.	...	...
1 per cent. glutinous rice starch solution, 100 cc.	2.0	2.6
1 per cent. erythrodextrin solution, 5.0 cc.	...	...

From the above results it can safely be concluded that, if glutinous rice starch contains a large quantity of erythrodextrin, the amount of baryta water to be used for a thorough precipitation of carbohydrates must be much greater than in case of potato or common rice starch. It will, however, be seen above that its value is quite close to that obtained in case of common rice starch. These results, as well as the consideration relative to the consistency of the paste, point to the probability that erythrodextrin does not exist in the glutinous rice starch.

As the author has stated elsewhere, achroödextrin is not precipitated by baryta water, while other dextrins and starches are precipitated by this reagent. This affords a convenient means of separation of achroödextrin from other carbohydrates. The author determined the minimum quantity of achroödextrin which can be detected in potato starch in the way already mentioned. The result was so very satisfactory that even less than 0.5 gram of achroödextrin in 100 grams of sample could be readily detected.

An attempt was next made to ascertain whether achroödextrin exists in glutinous rice starch in the following way: About 10 grams of glutinous rice starch were boiled with 100 cc. of water; after cooling, 400 cc. of saturated baryta water were added. After 48 hours the mixture deposited a white precipitate, leaving a clear supernatant solution. When the necessary quantity of 96 per cent. alcohol was added to the solution for precipitation of achroödextrin not even turbidity was noticed. This result shows that the glutinous rice starch does not contain achroödextrin.

ISOLATION OF THE HYDROLYZED PRODUCTS OF GLUTINOUS RICE STARCH.

It was found necessary to examine the products formed by the action of malt-diastase on glutinous rice starch. The saccharification was carried on at 55° C. with the diastase prepared from barley malt until the iodine reaction could no longer be observed. Dextrin was separated from this conversion product and purified by repeated precipitation with alcohol. The dextrin thus prepared was a white, gummy substance, soluble in water and not precipitated by baryta water. It gave no color with iodine and had very little action upon Fehling's solution. Its specific rotatory power $[\alpha]_D$ 3.95 was found to be 201.2. These facts show that the substance is achroödextrin.

From the conversion products, the author also obtained a sugar having an opticity of $[\alpha]_D$ 3.95–137.2 and a reducing power of K —64.3. When the sugar solution was treated with phenylhydrazine acetate, an osazone was formed which separated from the cold solution in the crystalline form, appearing as beautiful, long, flat plates under the microscope. After inversion, the sugar solution produced the characteristic glucosazone with phenylhydrazine acetate. It is therefore evident that the sugar is maltose. Thus, the conversion products by the action of malt diastase on glutinous rice starch are identical with those of common starch.

It is also worth mentioning that as the hydrolyzing action of the diastase on the glutinous rice starch paste proceeds, the red coloration by iodine becomes lighter and lighter and at the same time the reducing property of the product on copper oxide increases rapidly, and finally iodine ceases to give any more red color. Atkinson's statement that the presence of some peculiar albuminoid is responsible for the red coloration by iodine appears then to be incorrect. His view may also be refuted by the fact that the glutinous rice starch gives a bright red coloration with iodine solution even after it has been purified by treating with acid and alkali, in fact a still brighter red color than when albuminoid impurities were present. The author also examined the conversion products of glutinous-rice-starch using the koji-diastase and found that they consisted of glucose, maltose and dextrin. Glutinous-rice-starch was also hydrolyzed by a mineral acid to glucose.

RATIO OF DEXTRIN TO SUGAR IN THE CONVERSION PRODUCTS.

Several experiments have been carried out for the purpose of comparing the amounts of maltose and dextrin produced by the action of diastase on different kinds of starch.

Five grams, calculated as dried substance of each sample of starches obtained from different sources, were mixed with 20 cc. of water and then 60 cc. of boiling water added. The starch solution was heated upon the water bath to insure a thorough gelatinization of the starch, and after cooling was digested with 20 cc. of the malt extract (20 grams of malt in 100 cc. of water) at 55° C. Control experiments were made in each case with malt extract alone, and the corrected values for the starch conversions were obtained by subtracting from the total value the values found in the check solutions:

ONE HOUR'S SACCHARIFICATION.

Starch.	Sample taken. Grams.	Calculated as dried matter. Grams.	Solid in saccharified solution calculated from the density. Grams.	Composition of conversion products. Grams. Maltose.	Dextrin.	$[\alpha]_D$ 3.96 observed.	$[\alpha]_D$ 3.96[1] calculated.
Glutinous rice starch.	5.45	5.00	4.98	3.70	1.38	155.0°	155.37°
Potato starch.....	5.59	5.00	5.01	4.55	0.44	142.5	143.35
Soluble starch.....	5.86	5.00	5.00	4.58	0.43	144.3	143.49
Common rice starch..	5.80	5.00	4.87	3.99	0.92	149.9	149.80

THIRTY MINUTES' SACCHARIFICATION.

Glutinous rice starch.	5.45	5.0	4.92	3.28	1.82	162.0	161.23
Potato starch.....	5.59	5.0	5.05	4.00	1.08	150.9	151.60
Soluble starch.....	5.86	5.0	5.02	4.21	0.86	149.2	148.86

In these experiments, the coloration of glutinous rice starch by iodine disappeared most rapidly.

These figures distinctly show that the proportionality of the conversion products of glutinous rice starch differs entirely from those obtained from the other starches, the former containing the greatest amount of dextrin and the least of maltose.

This result also shows that Shimoyama's statement that glutinous rice starch contains a great amount of Nageli's amylodextrin is erroneous, because the amylodextrin ought to be, according to Brown and Morris,[2] hydrolyzed by malt-diastase completely to maltose.

The author obtained an impure amylodextrin by the continued action of 10 per cent. hydrochloric acid on ungelatinized potato starch for about eleven months, and examined the behavior of this substance with baryta water. The result was that Nageli's amylodextrin precipitated difficultly with baryta water. This fact shows also the non-existence of amylodextrin in glutinous rice starch which latter is readily precipitated by baryta water.

The author has also made a comparative study on the action of koji-diastase upon different kinds of starch; the results were that the iodine coloration of glutinous rice starch vanished most rapidly, while the amount of dextrin contained in the conversion products of glutinous rice starch was greater than that of the similar products of the other starches.

This peculiarity is to be attributed to the characteristic nature of glutinous-rice-starch, and it seems probable that the glutinous-rice-starch contains a greater amount of amylopectin or some analogous constituent, from which is produced a dextrin, more slowly hydrolyzed by diastase than the common starch.

[1] Factors employed were: $[\alpha]_D$ 138° for maltose, $[\alpha]_D$ 202° for dextrose.

[2] Brown and Morris, *J. Soc. Chem.*, **1889**, 449.

CONCLUSION.

The starch of glutinous rice is characterized by a red coloration with iodine. The microscopic characteristics of the starch granules and the hydrolyzed products do not appear to differ in any way from those of common rice starch. The starch of glutinous rice does not contain amylodextrin (Nageli's), erythrodextrin, and special albuminoids, which were by some investigators considered as the cause of the red coloration by iodine.

The author proposes the suggestion that the red coloration of that peculiar starch by iodine is probably to be attributed to the characteristic nature of the starch itself, which is capable of dissolving only a very minute amount of iodine, but not to the presence of other dextrins or albuminoids as propounded by other investigators. Moreover, the glutinous-rice-starch contains none of the common starch which is colored blue by iodine.

Another remarkable fact is that the glutinous-rice-starch is rapidly hydrolyzed by diastase to dextrin with the production of a less amount of maltose than in the case of potato or common rice starch. The author considers that the glutinous-rice-starch contains a greater amount of amylopectin or some analogous constituent, which produces a dextrin hydrolyzed more slowly by diastase than the ordinary starch.

It is very probable that there are many other cereals in nature, containing a similar variety of starch. The author found that glutinous millet starch behaves like glutinous-rice-starch. A similar starch has also been observed in "mochi-kibi," "morokoshi" and a variety of "kaoliang."

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THE EFFECT OF SULFUROUS ACID ON FERMENTATION ORGANISMS.[1]

By W. V. CRUESS.

Received April 18, 1912.

The effect of sulfurous acid on fermentation and on the quality and composition of wine depends to a very great extent upon its action on the organisms naturally occurring on the grapes. The natural fermentation of grape must is a mixed one brought about by wild yeasts, wine yeasts, and to a smaller degree by molds and bacteria. Several enologists[2] have claimed that the proper addition of SO_2 to must results in a selection of the ellipsoideus, or true wine yeast, and an elimination of other organisms so far as their activity during fermentation is concerned. This gives a cleaner fermentation and a sounder wine than would result from the same must untreated with SO_2. During the vintage of 1911, laboratory and winery tests were made to observe the effect of sulfurous acid on the microörganisms occurring on California grapes.

[1] This work was undertaken at the suggestion and under the general direction of Prof. F. T. Bioletti, Univ. Calif., College of Agriculture.

[2] F. T. Bioletti, *Bulletin* **213**, Univ. Calif. Expt. Sta.; A. Bouffard, *Progres Agricole et Viticole*, **34**, 221–6, 394–8; **31**, 18–21; J. Ventre, *Ibid.*, **42**, 262–71; Chancrin, *Le Vin*, pp. 33–4.

The following table is given to indicate the relative susceptibility to SO_2 of pure cultures of various organisms under the conditions of experiments carried out in the laboratory. The active cells in several flasks, each containing 500 cc. of must inoculated with some one of the organisms listed in the table, were counted by dilution in must agar agar. The must was then divided into 100 cc. portions in small bottles. To these 50, 100, 200 and 400 mg. per liter of SO_2 respectively in the form of $K_2S_2O_5$ were added. The cultures were then allowed to stand at room temperature (20° C.), for thirty-six hours when counts of the active cells were again made by dilution on must agar. In taking the samples it was necessary to shake the flasks in order to avoid any loss of cells due to settling out. A comparison of the active cells before and after exposure to SO_2 should give an idea of the relative susceptibility of the various organsims tested to SO_2.

TABLE I—RELATIVE RESISTANCE OF VARIOUS PURE CULTURES TO SO_2.

Organism.	SO_2 in mg. per liter.	Original No. of cells per cc.	Cells per cc. after 36 hours exposure to SO_2.
Burgundy wine yeast	50	20,000	640,000
	100	20,000	2,000,000
	200	20,000	310,000
	400	20,000	36,000
Apiculatus yeast from California grapes	50	150,000	200,000
	100	150,000	75,000
	200	150,000	56,000
	400	150,000	0
Penicillium from California grapes	50	120,000	40,000
	100	120,000	0
	200	120,000	0
	400	120,000	0
Aspergillus Niger from California grapes	50	450,000	120,000
	100	450,000	20,000
	200	450,000	30,000
	400	450,000	0
Wild yeast (pastorianus type) from California grapes	50	620,000	580,000
	100	620,000	6,000
	200	620,000	190
	400	620,000	0
Vinegar bacteria from California grapes	50	310,000	14,000
	100	310,000	300
	200	310,000	2
	400	310,000	0

An examination of the above table shows that the ellipsoideus yeast, represented by the Burgundy wine yeast, is far more resistant to the inhibiting effect of sulfurous acid than the other microörganisms tested. Its numbers were not diminished by any of the amounts of SO_2 used and only with the very large dose of 400 mg. per liter was its increase prevented.

The apiculatus was able to increase slightly in the presence of 50 mg. of total SO_2 per liter, but 100 mg. per liter greatly reduced its numbers, and after exposure to 400 mg. per liter none of the cells of this yeast were able to develop on nutrient agar.

The ordinary green mold, Penicillium is seen to be very susceptible to sulfurous acid, 50 mg. per liter of SO_2 diminishing the number of active cells from 120,000 per cc. to 40,000 per cc. and 100 mg. or over per litre completely inhibiting its growth under the conditions of the experiment.

The Aspergillus was considerably more resistant than the Penicillium since it took 400 mg. per liter of sulfurous acid to render all the cells incapable of developing. It is to be noted, however, that it did not increase in numbers during the exposure to any of the amounts used, indicating a decided inhibiting effect, even with such a small dose as 50 mg. SO_2 per liter.

The wild yeast of the pastorianus type was even more sensitive than the apiculatus yeast and was prevented from increasing by a dose of 50 mg. per liter of SO_2, 100 and 200 mg. of SO_2 per liter reduced the number of active cells and 400 mg. per liter rendered all of the cells incapable of growth when transferred to agar plates. Thus this type of wild yeast (very common on California grapes) is seen to be very susceptible to the inhibiting effect of SO_2.

The resistance of the vinegar bacteria culture used was very low, as 50 mg. of SO_2 per liter reduced the number of active cells 95.5 per cent., 100 mg. 99.9 per cent. and 200 mg. per liter rendered the must practically free from vinegar bacteria, capable of growth. None of the bacteria could develop after exposure to 400 mg. per liter of sulfurous acid.

The practical value of these differences in susceptibility to SO_2 is in cases where it is desired to ferment a must with the addition of pure yeast, or where a fermentation as free as possible from the active molds, apiculatus, and various wild yeasts is wanted. Müller-Thurgau[1] has shown that the apiculatus yeast is particularly harmful to the fermentation of ellipsoideus yeast. This is because it develops very rapidly, exhausts the nutriment that should go to the ellipsoideus yeast, and at the same time gives products that are injurious to the growth of the wine yeast. The apiculatus can be eliminated by doses of SO_2 that do not impair the vitality of the wine yeast. The green mold probably does very little harm during fermentation but it is especially troublesome when grapes are shipped a long distance to the winery, due to the fact that it attacks broken berries, giving a moldy taste and odor to the grapes. This difficulty can be obviated by crushing the grapes and hauling in tank cars in which the crushed grapes have been sulfited to prevent the development of the Penicillium. The aspergillus mold and the vinegar bacteria do little harm during fermentation and amounts of SO_2 that will remove the apiculatus and wild yeast will prevent the growth of the aspergillus and vinegar bacteria.

Tests made on fresh must and crushed grapes indicate that the ellipsoideus yeast occurring naturally on the grapes is more resistant to sulfurous acid than the other organisms associated with it. The following experiment was made on must from Palomino grapes that were especially moldy and broken, so that the results represent extreme conditions. The organisms in the fresh must were counted by dilution on nutrient agar. The must was then divided in 500 cc. portions among a series of quart jars and sulfited by the addition of $K_2S_2O_5$ to give the amounts of total SO_2 indicated. After three hours exposure to the sul-

[1] *Lafar Technical Mycology*, [2] **2**, 436–42.

furous acid, counts were again made on the active cells.

TABLE II.—EFFECT OF SO_2 ON ORGANISMS IN WHITE MUST (LABORATORY TEST.)

No. of flask.	Mg. SO_2 per liter added.	Mold cells per cc.	Apiculatus cells per cc.	Ellipsoideus cells per cc.
Original must no SO_2	00	97,625	7,341,400	58,575
1	32	13,310	189,030	182,995
2	79	19,360	21,380	33,880
3	127	14,651	14,651	43,953
4	190	7,600	00	58,400
5	253	4,800	00	73,600

The results demonstrate that very small amounts of sulfurous acid inhibit the increase of molds and apiculatus occurring naturally on the Palomino grapes in question. A moderate dose of 190 mg. per liter rendered all of the apiculatus cells exposed to it incapable of development when transferred to nutrient agar agar. The mold spores were more resistant, but were reduced in numbers in all cases. This indicates that they could do but little harm, since the ellipsoideus yeast would soon outgrow them and make the growth of the mold impossible by the exhaustion of the oxygen and the formation of alcohol. This conclusion is justified by the fact that the ellipsoideus yeast was not reduced in numbers by the amounts of SO_2 used above.

A test on a large vat of crushed grapes of the Zinfandel variety gave results similar to those on the Palomino must. The counts were made on average samples of the crushed grapes taken from the vat.

TABLE III.—EFFECT OF SO_2 ON ORGANISMS IN MUST FROM RED WINE GRAPES.

Sample.	Mold cells per cc.	Apiculatus cells per cc.	Wild yeast not apiculatus per cc.	Ellipsoideus yeast cells per cc.
Before sulfiting	1,600,000	2,830,000	30,000	120,000
One hour after sulfiting	None	None	None	560,000
After adding pure wine yeast	None	None	None	2,500,000

The molds and wild yeasts are seen to have been rendered incapable of developing after one hour's exposure to 120 mg. of SO_2 per liter. On the other hand the ellipsoideus yeast was apparently unaffected by the treatment, for it actually increased in numbers during this period. The addition of the pure Burgundy wine yeast greatly increased the number of wine yeast cells in the liquid. On sound grapes the numbers of ellipsoideus cells naturally present would be far less than indicated above, as these Zinfandel grapes had become moldy and broken during shipment to the winery. Thus in a normal must, that had been properly sulfited, the addition of the above amount of yeast (representing 1 per cent. of vigorously fermenting must) would insure a fermentation due almost entirely to the added yeast.

Sulfurous acid, usually in the form of potassium metabisulfite, is often employed for the defecation of white must to remove suspended solids. The effect of this practice on the organisms in the must is shown by the following tests:

TABLE IV.—EFFECT OF DEFECATION WITH SO_2 ON ORGANISMS IN MUST. Thompson seedless grapes; laboratory test.

Sample.	Mold cells per cc.	Yeast cells per cc.	Per cent. elimination of molds.	Per cent. elimination of yeast.
Original must	6,800	6,300	...	...
After 48 hrs. exposure to SO_2	None	11	100	99.84

TABLE V.—EFFECT OF DEFECATION ON ORGANISMS IN GREEN HUNGARIAN MUST. CELLAR TEST.

Sample.	Mold cells per cc.	Wild yeast cells per cc.	Ellipsoideus cells per cc.	Per cent. mold eliminated.	Per cent. wild yeast eliminated.	Per cent. ellipsoideus yeast eliminated.
Original must	29,262	8,603,000	29,262			
After 32 hrs. defecation with 250 mg. per liter SO_2	256	none	493	99.12	100	98.32

TABLE VI.—PALOMINO MUST. CELLAR TEST.

Sample.	Mold cells per cc.	Apiculatus cells per cc.	Ellipsoideus cells per cc.	Per cent. mold eliminated.	Per cent. apiculatus eliminated.	Per cent. ellipsoideus eliminated.
Original must	112,658	1,565,500	529,133	..	..	...
After 3 hrs. defecation	35,937	226,270	585,640	68 1	85.6	...
After 8 hrs. defecation	44	660	13,800	99.96	99.6	97.91
After 20 hrs. defecation	10	None	16,280	99.99	100	96.92

The results demonstrate that defecation by the use of sulfurous acid is very effective in delaying fermentation by removing or inhibiting the growth of fermentation organisms. This permits of removal of suspended matter by sedimentation. Here, as in Table I, the molds are found to be more susceptible to SO_2 than the ellipsoideus yeast. The apiculatus is seen to be even less resistant than the mold. After defecation the clear must should be drawn off and fermented by the addition of a pure culture of selected wine yeast. This will give a fermentation practically free from injurious wild yeasts and molds.

The following experiment illustrates the effect of defecation by the use of SO_2 as applied to apple must on a laboratory scale. A count was made on the fresh juice by dilution on nutrient agar. The must was then divided among several flasks in 150 cc. portions. The quantities of SO_2 indicated were added and after 72 hours, counts were again made on the active cells.

TABLE VII.—EFFECT OF DEFECATION BY USE OF SO_2 ON APPLE MUST OF NEWTOWN PIPPIN APPLES GROWN IN CALIFORNIA.

Flask.	Period of defecation.	SO_2 in mg. per liter.	Mold cells per cc.	Wild yeast cells per cc.	Ellipsoideus cells per cc.
1	0 hrs.	00	100,000	Large number[1]	Very few[1]
2	72	00	50,000	5,000,000	5,000,000
3	72	100	00	00	2,700
4	72	200	00	00	300
5	72	300	00	00	00
6	72	400	00	00	00

TABLE VIII.—COUNTS OF CELLS IN SEDIMENT OF TABLE VII.

Flask	Period of defecation.	SO_2 in mg. per liter.	Mold cells per cc.	Wild yeast cells per cc.	Ellipsoideus cells per cc.
3	72 hrs.	100	09	00	150,000
6	72 hrs.	400	00	00	1,200

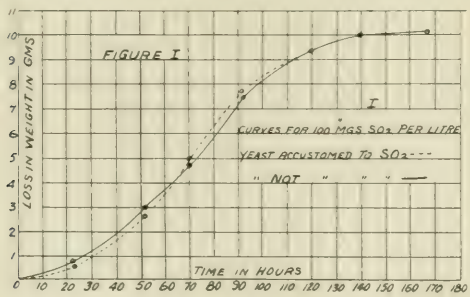
The counts in Table VII were made from the supernatant liquid and in Table VIII from the sediment. The

[1] The large number of mold cells present in must prevented a count of yeast colonies.

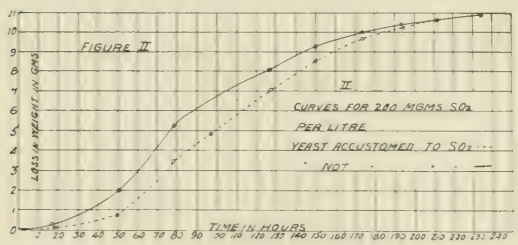
figures indicate that defecation by the use of sulfurous acid would be beneficial in the treatment of apple must, since it would result in the elimination of molds and wild yeasts and permit of fermenting the cider by the addition of pure selected cider yeast, after drawing off the defecated liquid. By comparing the results of Tables VII and VIII it is seen that the elimination of the ellipsoideus cells is largely due to settling out, whereas the effect on the molds and wild yeasts is due to the direct action of the sulfurous acid, since the number of ellipsoideus cells is greater in the sediment than in the supernatant liquid and the numbers of molds and wild yeasts are 00 in both cases.

Some investigators have thought that the yeast that survives a given dose of sulfurous acid becomes more resistant to its effect. Taking this view, the ellipsoideus yeast that developed after sulfiting in the above tests would be a yeast accustomed to SO_2. To observe whether such an effect is produced a number of tests were made.

Burgundy wine yeast was grown in the presence of 100 mg. of sulfurous acid per liter. When in active fermentation 1 cc. of this culture was transferred to 150 cc. of must containing 100 mg. per liter of SO_2. A similar amount of must containing 100 mg. per liter of SO_2 was inoculated with 1 cc. of a vigorous culture of Burgundy wine yeast, grown in must to which no

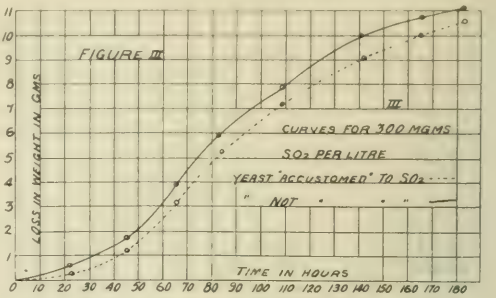


sulfurous acid had been added. The flasks were incubated at 32° C. and the rates of fermentation, as indicated by loss in weight, observed. The yeast, supposedly accustomed to SO_2, was then transferred to must containing 200 mg. per liter of sulfurous acid. When in vigorous fermentation 1 cc. of this culture was transferred to 150 cc. of must containing 200 mg.



per liter of SO_2. A check flask containing 200 mg. per liter of SO_2 was inoculated with 1 cc. of a culture of Burgundy yeast unaccustomed to SO_2. The rates of fermentation were observed in each case. The above process was repeated in every respect with 300 mg. per liter of SO_2. The results of the tests are given in the accompanying curves.

At 100 mg. per liter the "yeast accustomed to SO_2" and the normal yeast gave practically the same kind of a fermentation. At 200 mg. per liter the yeast "accustomed to sulfurous acid" started more slowly than the other but finished in the same time. This indicates an increased susceptibility to SO_2, but



not any decrease in fermentative activity. At 300 mg. the yeast "trained" to SO_2 showed a slower start of fermentation and a slower fermentation throughout. It is to be noted that the curve for the "accustomed" yeast in Fig. III does not cut the curve of the normal yeast during the fermentation period of the latter, although if the test had been carried far enough it would probably have done so. The curves, as they stand, show that the yeast unaccustomed to sulfurous acid had finished fermenting, whereas the other had not, at the end of the test. This indicates an increased susceptibility to SO_2 as well as a decrease in vitality, due no doubt to the long exposure to sulfurous acid. A number of similar laboratory tests of a qualitative nature bring out the same general features as indicated in the above tests, namely, that wine yeast (as typified by the Burgundy yeast) does not become accustomed to the action of sulfurous acid upon prolonged exposure to SO_2 in must, but tends to become more susceptible to it.

A test was made on the change of susceptibility to sulfurous acid of Burgundy wine yeast used at a winery during a vintage of six weeks. This yeast had been grown in must sulfited to remove the injurious organisms and theoretically should have become thoroughly accustomed to the effect of SO_2. The must in which it grew usually contained about 200 mg. per liter of sulfurous acid added in the form of $K_2S_2O_5$. This must was renewed at least once in every 24–72 hours so that the yeast was kept in a vigorous condition.

A series of flasks each containing 300 cc. of sterile must was inoculated with 1 per cent. of vigorously fermenting liquid from the yeast apparatus. The amounts of SO_2 indicated in the table were added in the form of $K_2S_2O_5$. A similar series with corresponding amounts of sulfurous acid was inoculated with the same variety of yeast, but yeast which had not been grown in the presence of SO_2. The rates of fermentation were observed in each flask.

TABLE IX.—SERIES I. YEAST NOT ACCUSTOMED TO SO_2.[1]

Date.	Hours.	Balling of flask A_1 100 mg. SO_2 per liter.	Balling of flask B_1 150 mg. SO_2 per liter.	Balling of flask C_1 200 mg. SO_2 per liter.
10/19/11 3 P.M.	00	25 1/4	25 1/4	25 1/4
10/20/11 8 A.M.	17	25 1/4	25 1/4	25 1/4
10/21/11 8 A.M.	41	25 1/4	25 1/4	25 1/4
10/22/11 8 A.M.	65	25 1/4	25 1/4	25 1/4
10/23/11 8 A.M.	89	25 1/4	25 1/4	25 1/4
10/23/11 6 P.M.	99	25 1/4	25 1/4	25 1/4
10/24/11 8 A.M.	113	24.9	25 1/4	25 1/4
10/25/11 10 A.M.	139	24	25 1/4	25 1/4
10/26/11 10 A.M.	163	18	25	25
10/27/11 10 A.M.	187	13.5	20	21
10/28/11 2 P.M.	215	6	10.5	14
10/29/11 9 A.M.	234	3.5	7	8.5
10/30/11 9 A.M.	258	0.5	4	5
10/31/11 10 A.M.	283	0	0.75	1
11/1/11 10 A.M.	307	0	0	0

[1] Slow start of fermentation was due to fact that no incubator was available at winery so that the temperature was too low for rapid start of fermentation.

TABLE X.—SERIES, II YEAST "ACCUSTOMED" TO SO_2.

Date.	Hours.	Balling of flask A_2 100 mg. SO_2 per liter	Balling of flask B_2 150 mg. SO_2 per liter	Balling of flask C_2 200 mg SO_2 per liter.
10/19/11 3 P.M.	0	25 1/4	25 1/4	25 1/4
10/20/11 8 A.M.	17	25 1/4	25 1/4	25 1/4
10/21/11 8 A.M.	41	25 1/4	25 1/4	25 1/4
10/22/11 8 A.M.	65	25 1/4	25 1/4	25 1/4
10/23/11 8 A.M.	89	25 1/4	25 1/4	25 1/4
10/24/11 8 A.M.	113	25	25 1/4	25 1/4
10/25/11 10 A.M.	139	24	25 1/4	25 1/4
10/26/11 10 A.M.	163	16	25 1/4	25 1/4
10/27/11 10 A.M.	187	11.5	25 1/4	25 1/4
10/28/11 2 P.M.	215	5	25 1/4	25 1/4
10/29/11 9 A.M.	234	2.5	25 1/4	25 1/4
10/30/11 9 A.M.	258	0	25 1/4	25 1/4

The results are decidedly in favor of the yeast unaccustomed to sulfurous acid. Flasks B_2 and C_2 of the series with the "accustomed" yeast did not ferment, whereas the corresponding flasks A_1 and B_1 in the other series fermented out dry. A_2, however, fermented just as rapidly as A_1. This indicates that the yeast grown in the presence of SO_2 in the pure yeast apparatus had become more susceptible to the inhibiting action of SO_2, but where fermentation took place its rate of fermentation had not become reduced.

SUMMARY.

From the observations given it is seen that sulfurous acid may be used to advantage in inhibiting the growth of wild yeast molds, and vinegar bacteria, such as occur on California grapes and at the same time permit the vigorous development of the true wine yeast Saccharomyces ellipsoideus, naturally on the grapes, or added as starter.

Wine yeast can not be trained to become more resistant to SO_2 in appreciable quantities. Therefore, the present idea of going through a troublesome process of "accustoming" wine yeast to SO_2 does not seem to be based on the proper principles. A better way, no doubt, would be to sulfite the must to be fermented in order to eliminate molds, wild yeasts, etc., and then ferment it with a starter of pure wine yeast (or if it is apple juice, with pure cider yeast) that has been grown in musts free from sulfurous acid.

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CONCERNING THE SUGAR CONTENT OF WATERMELONS.

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Received January 24, 1912.

The literature on the sugar content of watermelons is comparatively meagre. Wiley[1] has examined the sugar content of melons, and for the average reducing sugar content of watermelons has reported it as 4.33 per cent. of the meat-juice and 2.47 per cent. of the rind-juice. He reported the sucrose content as 1.92 per cent. of the meat-juice and 0.34 per cent. of the rind-juice. The ash value was given as 0.31 per cent. of the juice from the meat and 0.38 per cent. of the juice from the rind. Kremla,[2] by six different determinations, found the reducing sugar content to be 4.19 grams sugar per 100 cc. of the juice. Nardini[3] reported the following results from the Italian Experiment Station: Invert sugar, 4.94 per cent.; sucrose, 0.765 per cent.; ash, 0.168 per cent. Jaffa,[4] from the California Experiment Station, reported the ash content of the total melon as 1.41 per cent.

At the time our investigation was started we had access to melons that seemed sweeter than the usual melons found on the market. Since other chemists had made no statements showing that the melons they had examined were other than the average market melons, it seemed desirable to investigate these apparently sweeter melons and determine their sugar content. The melons were the usual melons grown in the vicinity of Bloomington, Indiana; they had very thin rinds and were less desirable melons, owing to the ease with which they were broken during shipment to market.

In the course of the investigation we studied the ratio of juice to pulp and rind; some work was done on the ash content of the juice, but the main work had to do with the sugars present in the strained juice. We were interested in the alcohol and acetic acid, respectively, that could be produced by the fermentation of the juice, and some results of that phase of the investigation are given. In order to carry on the work, about a dozen medium-sized melons were procured near the end of the season and were preserved by cutting the melon with a silver knife and scraping the juice and pulp by means of a watch glass—as long as any red meat remained attached to the rind. The juicy pulp was filtered in some cases through paper, but this became a very tedious process, owing to the tenacious silt, so the major part of the juice was simply strained through a well-washed cheesecloth and collected in quart bottles and liter flasks. These were plugged with cotton and immediately sterilized in a bacteriological autoclave at a pressure of 16 to 18 pounds for 30 minutes.

[1] Wiley, U. S. Dept. of Agriculture, *Report*, **1886**, 345.

[2] Kremla, *Chemie der menschlichen Nahrungs- und Genussmittel*, edit 4, 1904, **1**, 1496; **2**, 921.

[3] Nardini, *Ibid.*, **1**, 1496

[4] Jaffa, *Ibid.*

The various vessels were then removed, capped with sealing-wax and allowed to stand in a dark cupboard. With scarcely any exceptions the juice remained perfectly sterile until needed. In the bottom of each bottle was a small precipitate (white in the filtered sample, reddish brown in the strained sample) of coagulated material. This was very likely of a protein nature but it was not investigated. A few samples of the juice that had been neutralized before heating were slightly brown in color after the sterilization.

Eleven different juices, not counting several modifications of a single juice in a few instances, were carried through the various analytical processes employed.

No. 1 was the natural juice, acid in reaction, strained and filtered.

No. 2A was the strained juice of a melon that had been cracked, apparently very shortly before arrival at the laboratory.

No. 2B and 2C were from the same melon, which was quite ripe and in good condition. The juice 2B was strained and neutralized with sodium hydroxide solution. After heating, this juice was dark in color. The juice 2C, already acid in reaction, was strained and filtered through paper. This juice yielded no residue after sterilization.

No. 3 was the natural juice taken from an average melon.

No. 4A was also the juice from a melon quite the average of the lot.

No. 4 and 4N were taken from the same melon. The former was allowed to remain naturally acid, while the latter was neutralized before sterilization. The melon was ripe.

No. 5 was the juice from an average melon strained and left acid in reaction.

No. 6 was the juice from a melon which was slightly green. This juice yielded no residue on heating.

No. 7 and No. 8 were the juices from the two poorest melons—strained only.

No. 9A and No. 9B were duplicated from the same melon which was perhaps the best in the lot. The 9A juice was left acid. Juice 9B was filtered and the filtrate, also left acid in reaction, was clearer than No. 9A.

No. 10 and No. 10A were juices from two different average melons. In each case the acid juice was strained.

No. 11 and No. 11A were from the same melon. Both samples were strained: the former was allowed to remain acid in reaction while the latter juice was made neutral.

In the respective juices, the solids were determined by means of the Brix hydrometer (column II) with the filtered juice at the ordinary temperature. The results include the temperature correction. The solids in terms of cane sugar were sought in a portion of the juice by means of the immersion refractometer. The values depending on the refraction of the mixture (column III) were obtained by use of freshly-opened filtered juice. Temperature corrections are included in the results. Portions of the juices examined with the hydrometer and refractometer were defecated and again examined with the refractometer. In the defecation, 100 cc. of the juice were placed in a 200 cc. graduated flask. Several drops of basic lead acetate solution were added, the flask being carefully shaken after the addition of each drop of the reagent. When a yellowish white precipitate settled out, leaving a water-clear solution, three to five drops of glacial acetic acid were added. A good excess of lead acetate gave harmful results, so it was avoided. The defecated juice was diluted to the mark and filtered. By this method the filtrates were always well clarified. The total solids in terms of cane sugar, obtained by the use of the Zeiss immersion refractometer on the defecated juice, are shown in column IV.

TOTAL SOLIDS IN TERMS OF PER CENT CANE SUGAR.

	I.	II.	III.	IV.
Sample	1	9.02	9.05	9.62
	2C	9.64	9.51	8.10
	2B	9.57	9.58	10.16
	2A	9.62	9.90	10.10
	3	9.23	9.75	11.76
	4A	10.26	10.49	10.96
	4	9.42	10.25	10.68
	5	8.42	6.72	7.76
	6	9.52	9.50	8.42
	4N	9.82	10.28	10.76
	9A	8.63	8.74	9.48
	9B	9.07	9.02	9.56

The results in columns III and IV are based on Wagner's "Tabellen für Zeiss Eintauschen Refractometer" and include corrections for the instrument and the temperature employed.

SUCROSE.

The determination of the sucrose was brought about by means of the polariscope both before and after inversion of the defecated juice. The per cent. sucrose (column II) was calculated from the Clerget formula:

$$\text{Per cent. sucrose} = \frac{100\,(\text{Direct} - \text{Invert reading})}{142.66 - \frac{T}{2}}$$

In column III is given the per cent. sucrose found by the Fehling titration method (sucrose equivalent to the reducing sugars resulting from inversion, minus the reducing sugars found present prior to inversion). Column IV shows the same data expressed in terms of grams sucrose per 100 cc. of juice.

The method employed in the inversion of the sucrose was as follows: 50 cc. of the defecated juice which had been freed from lead salts were placed in a 100 cc. graduated flask; 25 cc. of water were added and then, while constantly rotating the flask, 5 cc. 38.8 per cent. HCl were slowly added. The flask was placed in a water bath already heated to 70° C. and the juice heated to 68–70° C. in approximately three minutes. The heating at this temperature was continued for about seven minutes. The flask was then removed from the bath and cooled to 20°–21° C. and diluted to 100 cc. Readings were taken with a decimeter tube and the readings were multiplied by 2 and calculated by the general formula given earlier in this paper.

	I.	II.	III.	IV.
Sample	1	0.9972	0.820	0.892
	2C	0.732	0.840	0.916
	2B	0.973	1.141	1.468
	2A	0.729	0.811	0.898
	3	too dark	0.993	1.084
	4A	0.920	1.149	1.230
	4	1.119	1.102	1.204
	5	1.599	1.550	1.789
	6	1.416	1.404	1.533
	4N	too dark	0.847	0.928
	9A	1.639	1.617	2.011
	9B	1.543	1.613	1.873
	10A	0.757	...	0.905
	10	1.101	...	1.434
	11A	1.592	...	1.846
	11	0.7669	...	0.988
	8	0.733	...	1.066
	7	0.720	...	0.990

REDUCING SUGARS.

The defecated juices obtained in the previous determinations were allowed to act on Fehling's solution in the usual way. Five cc. each of the alkali and copper solution were measured by a pipette to an Erlenmeyer flask, diluted with 40 cc. water brought to boiling and then allowed to react with the defecated juice. No indicator was used. The various sugar solutions gave the following results expressed in grams reducing sugar per 100 cc. of juice:

Sample	1	5.678
	2C	5.510
	2B	5.514
	2A	5.969
	3	4.343
	4A	4.313
	4	5.037
	5	5.163
	6	5.485
	4N	4.580
	7	5.687
	8	4.504
	9A	4.846
	9B	4.692

ACETIC ACID AND ALCOHOL.

After obtaining the foregoing sugar data it seemed desirable to ascertain the amount of alcohol and acetic acid, respectively, that could be obtained by the fermentation of the respective sugar solutions. These fermentations were carried out at 34°–35° C., and after distillation the alcohol and acetic acid recovered from each fermentation mixture were estimated by means of the Zeiss immersion refractometer. All results include corrections for the temperature and the instrument and are based on Wagner's "Tabellen." Owing to the rush of other work at the time this work was in progress we could not check the alcohol determinations by the specific gravity method nor the acetic acid by the titration method. The refractometer results are given for what they are worth. Column II shows the per cent. alcohol by weight in a given volume of liquid that was recoverable from the same volume of the corresponding juice. Column III shows the per cent. acetic acid by weight of a solution resulting from the fermentation of a similar quantity of the corresponding melon juice. In the alcohol distillations the usual precautions regarding the constant volume of the distilling mixture and the presence of calcium carbonate were observed. In the acetic acid distillations the same precautions regarding constant volume and the presence of phosphoric acid were used:

	I.	II.	III.
Sample	1	2.45	1.86
	2C	2.95	1.98
	2B	1.87	2.18
	2A	2.36	1.69
	3	2.70	1.27
	4	1.03	1.91
	4A	2.70	1.69
	4N	2.06	1.69
	5	1.84	1.74
	6	2.12	1.87
	9A	3.06	lost
	9B	2.85	lost
	10A	2.73	lost
	11	2.29	1.69
	11A	2.39	1.54

In working up the melons our main efforts were directed in preserving the juice and incidentally we became interested in finding the ratio of pulp and rind to juice. The pulp and rind were weighed just after pressing, and the following results were obtained on a few of the average melons:

Sample.	Juice, Per cent.	Rind, Per cent.	Pulp, Per cent.	Total melon weight (grams).
3	41.2	49.7	9.1	6250
4	42.9	45.1	12.0	7250
5	42.5	47.1	10.5	7590
7	42.9	50.9	7.2	6000
8	51.5	41.4	7.1	4820

Although the above figures are only approximate it seems that a melon reasonably ripe and having a comparatively thin rind is about 40 per cent. juice. (Number 8 was an exceptional melon.)

PENTOSES.

With regard to the pentose content of the juice the investigations indicated that only a small amount of pentoses were present. Of Sample 2C, 50 cc. were boiled with HCl in the usual way, distilled and the distillate converted into the phloroglucid which was weighed. The latter corresponded to only 0.00236 gram pentose in the sample taken. No further work was done with the small amount of pentoses present.

ASH CONTENT.

The ash of three samples of the juice was investigated. The residue, on evaporation of the juice, was sulphated by the addition of 10 cc. conc. H_2SO_4 to the residue from 100 cc. of the juice. This sulphated juice was taken up in water, the insoluble portion again sulphated, extracted with water and the insoluble part weighed after ignition. The united extracts were evaporated and weighed:

Sample of juice.	Per cent. soluble ash.	Per cent. insoluble ash.
1	0.2328	0.038
2C	0.2019	0.02+
3	0.2103	0.030

CONCLUSIONS.

1. The melons examined were about 43 per cent. juice, 47 per cent. rind and 10 per cent. pulp.

2. The ash content was near 0.25 per cent. of the juice; of the ash, about one-eighth was insoluble.

3. On fermentation, the sugar present yielded an alcoholic solution containing about 2.5 per cent. alcohol by weight.

4. There could be obtained from the fermented melon juice an acetic acid solution that was about 1.75 per cent. pure acid.

5. The reducing sugars, by the Fehling titration method, were found to run near 5.5 per cent. of the juice. By the polariscope they were found in a smaller quantity usually. We are unable to explain the fact that the two methods do not run closer together. It would seem that the lead acetate defecation did not take out all the substances in the juice that might reduce Fehling's solution.

6. Usually more than 1.00 per cent. of the juice was sucrose.

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THE DETERMINATION OF BENZALDEHYDE IN MARASCHINO CHERRIES AND MARASCHINO LIQUEUR.

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Received April 9, 1912.

Comparatively recent investigations by food authorities into the composition of Maraschino cherries, and the possibility of distinguishing the genuine product from artificial imitations, have made desirable a method for the determination of small amounts of benzaldehyde, a common ingredient of food products of this nature.

For this purpose the method of determining benzaldehyde as the phenylhydrazone, originally proposed by Fischer[1] and adapted to the examination of almond extracts by Denis and Dunbar,[2] suggested itself. It was evident almost from the beginning, however, that this method, although satisfactory for the comparatively large amounts (0.1 gram) of benzaldehyde present in almond extracts, is not suitable for quantities as small as five milligrams, as found in Maraschino cherries. This is clearly shown in Table I, which gives the results obtained by the Denis and Dunbar method on known amounts of redistilled benzaldehyde dissolved in 95 per cent. alcohol. Blank determinations to correct for the effect of the reagent were made at the same time. The precipitate obtained in each case in the blank determination was of a gummy, resinous character, as was true also of the determinations involving the smaller amounts of benzaldehyde.

TABLE I.—RESULTS OBTAINED BY THE DENIS ABD DUNBAR METHOD.

Mg. benzaldehyde taken.	Mg. ppt. obtained.	Equivalent mg. benzaldehyde.	Per cent. of theory.	Mg. ppt. in blanks.
29.3	53.7	27.4	93.61	3.1
4.965	9.7	5.248	105.7	3.0
4.965	8.8	4.761	95.9	3.0
4.740	9.1	4.922	104.0	3.9
9.480	16.3	8.818	93.09	3.9

As shown in the table, the lowest value for the blanks was three milligrams, or almost 30 per cent. of the total weight of precipitate when five milligrams of benzaldehyde were present. The results differ quite widely, some being above and some below the theoretical value.

[1] *Z. anal. Chem.*, **25**, 230 (1885).
[2] THIS JOURNAL, **1909**, 256.

Further study of the method as applied to small amounts of benzaldehyde showed that the precipitation was markedly affected by several distinct factors. A high percentage of alcohol retarded or even prevented the precipitation, while too little alcohol tended to make the precipitates gummy instead of crystalline. The best results were obtained when the alcohol amounted to about ten per cent. by volume. It was found also that the weight obtained in the blank determinations was proportional to the length of time that the solutions stood after adding the reagent and before filtering, being reduced from 3.0 milligrams to 0.3 milligram for half an hour's standing. The character of the precipitate varied also with the length of time that the solution stood, being much lighter in color for the shorter time. The results obtained with known amounts of benzaldehyde by precipitating and allowing the solution to stand for half an hour were, however, too low, showing incomplete precipitation. It was found possible, however, to secure complete precipitation in ten minutes by shaking the solution in a stoppered flask after the addition of the reagent. About 95 to 97 per cent. of the theoretical values were obtained with five milligrams of benzaldehyde, while the weight of the blank did not exceed 0.5 milligram for 10 cc. of reagent. Some of the results obtained under these varying conditions are shown in Table II.

TABLE II.—EFFECT OF VARYING CONDITIONS ON THE PRECIPITATION OF BENZALDEHYDE.

Mgs. benzaldehyde taken.	Mgs. ppt. (corrected).	Equivalent benzaldehyde.	Per cent. of theory.	Conditions of precipitation.
7.097	12.10	6.546	92.26	20 per cent. alcohol.
7.097	12.00	6.492	91.49	20 per cent. alcohol.
7.097	12.00	6.492	91.49	30 per cent. alcohol.
7.097	11.70	6.330	89.21	30 per cent. alcohol.
5.359	11.70	6.330	118.1	1 per cent. alcohol
5.359	11.40	6.167	115.1	1 per cent. alcohol.
6.780	11.80	6.384	94.17	10 per cent. alcohol and 30 mg. acetaldehyde.
6.780	11.60	6.276	92.43	10 per cent. alcohol and 30 mg. acetaldehyde.
5.707	9.70	5.248	91.96	10 per cent. alcohol shaken 5 minutes with reagent.
5.707	9.20	4.977	87.22	10 per cent. alcohol stood over night before adding reagent.
6.690	10.60	5.735	85.72	
6.690	10.80	5.842	87.34	10 per cent. alcohol, total volume
6.700	10.80	5.842	87.20	200 cc.
6.700	10.80	5.842	87.20	

To summarize these results briefly: The amount of alcohol present during the precipitation should be between 8 and 12 per cent. by volume. With 20 per cent. or more, the precipitation is incomplete, as might be predicted from considerations of solubility, no precipitation taking place at all with 50 per cent. of alcohol present. Too small an amount of alcohol tends to cause decomposition of the reagent, with consequent too high values for both the blanks and the benzaldehyde determinations. The presence of acetaldehyde has practically no effect on the precipitation, which is borne out by the fact that when acetaldehyde was present the blank determinations gave an increase of only 0.1 milligram over the 0.5 milligram usually obtained. Since the other alde-

hydes of this series are closely related to acetaldehyde in their chemical properties, it may fairly be assumed that the presence of aliphatic aldehydes,[1] which are the ones most likely to be present in liqueurs like Maraschino, exercises no deleterious effect. On account of the relative solubility of benzaldehyde-phenylhydrazone, the volume of solution for precipitation should not exceed 110 cc.

From the above considerations and based on the experience gained in more than one hundred determinations on known amounts of benzaldehyde, the following procedure is recommended for its determination in Maraschino cherries and Maraschino liqueur.

Dilute 100 cc. of the liquor from Maraschino cherries, or 50 cc. of Maraschino liqueur to 140 cc. in a 500 cc. flask and distil 110 cc. Determine approximately the alcohol in the distillate, filtered if necessary, by the pycnometer or immersion refractometer. Transfer 100 cc. of the distillate to a 300 cc. Erlenmeyer flask and add alcohol or water, as may be necessary, so that the solution shall contain approximately ten per cent. of alcohol by volume. Add 100 cc. of the reagent prepared as directed below, stopper tightly with a rubber stopper, and shake vigorously for ten minutes. Remove any precipitate adhering to the stopper, and filter on a tared Gooch crucible, washing with cold water, and finally with about ten cc. of ten per cent. alcohol. Dry in a vacuum desiccator for 20–24 hours at about 20 cm. pressure, or, if preferred, in a vacuum oven at 70°–80° C. for three hours. The precipitate should be kept from strong light as far as possible. A blank determination must be run at the same time, deducting the weight obtained from that of the precipitate. With our reagent this blank has been usually 0.0005 gram. The corrected weight of the precipitate, multiplied by 0.5411, gives the weight of benzaldehyde.

Reagent.—Mix 3 cc. of glacial acetic acid with 40 cc. of water, add 2 cc. of phenylhydrazine, shake thoroughly, and filter the emulsion through several thicknesses of filter paper. The clear filtrate should be used immediately, as standing over five minutes gives a turbid reagent.

The phenylhydrazine should be chemically pure, free as far as possible from dark color and turbidity. Frequent agitation of the precipitate during filtration through a rotary motion of the flask prevents it from sticking to the sides. The determination of the benzaldehyde in the distillate should be carried out without delay to prevent loss by oxidation.

Table III.—Benzaldehyde in 10 Per Cent. Alcohol.

Mg. benzaldehyde taken.	Mg. ppt. obtained (corrected).	Equivalent benzaldehyde.	Per cent. of theory.
5.359	9.5	5.140	95.90
6.363	11.5	6.212	97.77
6.595	11.7	6.330	95.98
48.30	86.8	46.96	97.23
81.80	146.7	79.38	97.03
5.408	9.5	5.140	94.99
8.230	14.6	7.900	95.98
9.930	17.6	9.521	95.90
81.12	144.8	78.34	96.58
81.12	145.0	78.45	96.72

The method can be applied to the determination of benzaldehyde in almond extracts, using 10 cc. of the extract diluted to 100 cc. with water, and 15 cc. of the reagent.

Typical results on known amounts of benzaldehyde by this method are shown in Table III.

The first six of the results in the table were obtained by direct determination on solutions of pure benzaldehyde. The remaining ones were distilled as directed in the procedure. Experimental evidence has shown that these dilute solutions of benzaldehyde can be distilled without material oxidation. Distilling in a current of carbon dioxide was tried but found to offer no advantage. The presence of considerable amounts of reducing sugars and sulphurous acid did not appreciably affect the distillation or determination.

The benzaldehyde content of some of the "Maraschino Cherries" and "Maraschino" liqueur on the market is shown in the following table:

Table IV.—Benzaldehyde Content of Commercial Samples of Cherries.

Brand.	Alcohol by volume.	Corrected wt. of precipitate.	Benzaldehyde. Mg. in 100 cc.
"Rosebuds"	0.0	8.70[1]	5.177
"Touraine"	0.0	53.00[1]	31.54
"Magnolia"	0.0	128.60[1]	76.54
Dandicolle & Gaudin	2.09	38.30	22.79
"Regina"	1.73	31.70	18.87
"Dupont"	4.97	53.90	32.07
"Bigarreaux"	4.27	20.40	14.29
Dalidet & Co.	7.96	14.30	8.509
Ginter Co.	0.0	16.00	10.58
"Percer"	6.19	60.60	36.07
Middleby Co.	0.0	6.900	4.106
Maraschino.			
G. Luxardo	32.60	. .	3.57
Richelieux	25.94	. . .	17.02
Marie Brizard & Roger	28.97	. . .	0.0
Cusenier (cherry liqueur)	32.63	. . .	12.01
Cusenier (Maraschino)	19.00	. . .	0.0
Nuyens et Cie	24.78	. . .	1.78
H. Shufeldt & Co., Peoria, Ill.	30.60	. . .	41.3

[1] In the case of some samples which contained extract of syringa, the precipitate was colored orange-red, but was calculated as benzaldehyde.

Genuine Maraschino, apparently, has a very low content of benzaldehyde. Consequently, Maraschino cherries, which show a relatively large amount of benzaldehyde, are in all probability artificially flavored. Determinations of benzaldehyde on unflavored cherries have shown that more benzaldehyde would come from the cherries, themselves, than from genuine Maraschino added as a flavoring agent. However, the former does not exceed 3–4 milligrams per 100 grams of cherries. In general, then, it might be said that in a sample of cherries flavored with genuine Maraschino liqueur, the benzaldehyde, expressed in milligrams per 100 cc. of the liqueur, should not be more than two or three times the alcohol content, expressed in per cent. of volume. Samples containing practically no alcohol and above 20 mg. of benzaldehyde are evidently entirely artificial.

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COMMERCIAL CINNAMON AND CASSIA.

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Received May 14, 1912

The varieties of cinnamon and cassia on the market are rather numerous, and differ from each other considerably in flavor, strength, ash, volatile oil, alcohol extract, etc. Considering these differences it seems of interest to tabulate the composition of some of the more important varieties as shown by average samples of large lots ground in the commercial way. Among the commonest used are broken China, Ceylon chips, broken Batavia, Saigon and Seychelle cassia. In addition, some data are given on some cinnamons and cassias not so well known. Broken China is Cassia cinnamon,[1] sometimes known as China cassia or Canton cassia, and is cultivated in the southeastern provinces of the Chinese Empire and exported by the way of Calcutta. It occurs in quills usually shorter than those of Saigon. The bark is aromatic, and somewhat astringent. It is imported in large rattan bales, and used extensively in commerce. Ceylon cinnamon is collected from *Cinnamomum zeylaniuum*,[1] indigenous to and cultivated in the island of Ceylon. It comes in closely rolled double quills, composed of numerous thin layers of the inner bark of the shoots. The odor is delicately aromatic, and very distinct from either Cassia or Saigon bark. Ceylon chips consist of the small refuse of the whole bark, and apparently the great amount of dirt present is due to the fact that these pieces are collected off the ground for shipment. Ceylon chips are imported in large and heavy bales packed by a press. Its use in commerce is very limited on account of its dirty condition. Ceylon cinnamon contains from 0.5 to 1 per cent. volatile oil. Batavia cassia is the bark of *Cinnamomum Burmanni*.[1] It occurs in double quills, the larger sometimes enclosing the smaller quills, 5–8 cm. long, outer surface light or reddish brown, nearly smooth, inner surface dark brown with occasional depressed areas, odor and taste aromatic and distinctly mucilaginous. Broken Batavia consists of quills broken in small pieces, and is imported very clean in ordinary bagging and used extensively in commerce. Saigon cassia is obtained from *Cinnamomum Loureirii*,[1] and is cultivated in Cochin China, and parts of China, and exported from Saigon in bundles about 30–40 cm. long, 20 cm. wide, and 10 cm. thick, weighing about 1.5–2 kg., and consisting of pieces varying in size and color from small brownish black single quills to large thick grayish-brown transversely curved pieces. The odor is aromatic, taste mucilaginous, aromatic and pungent. It is used very extensively in commerce, is imported in wooden boxes covered with rattan, and is usually clean. Seychelle cassia comes from the islands of that name in the Indian Ocean. It is a very thick bark, mild in flavor and odor, and exceedingly clean. It is imported in ordinary bagging.

Table I gives the average, maximum, and minimum of total ash and acid insoluble ash, by years, of samples from large lots. The A. O. A. C. methods of analysis were used.

[1] Kraemer's "Botany and Pharmacognosy," 2nd Ed., pp. 513–16.

Table I.—Percentages.

Variety	Samples	Total ash Max.	Min.	Av.	Ash insoluble in HCl Max.	Min.	Av.
Year 1908							
Broken China	(24)	7.47	3.12	4.79	4.17	0.69	2.02
Ceylon chips	(4)	7.60	7.38	7.47	3.80	3.02	3.59
Broken Batavia	(5)	5.00	4.31	4.68	1.71	1.13	1.40
Saigon	(9)	4.52	3.63	4.25	1.52	0.58	1.09
Seychelle	(4)	5.91	3.63	4.70	1.70	0.05	0.90
Year 1909							
Broken China	(15)	4.26	3.37	3.77	1.53	0.94	1.20
Ceylon chips	(4)	13.41	7.83	10.49	8.16	3.25	5.57
Broken Batavia	(2)	3.96	3.63	3.79	0.19	0.16	0.18
Saigon	(2)	4.36	4.22	4.28	1.71	0.78	1.24
Seychelle	(6)	4.90	3.42	4.40	0.27	0.03	0.11
Year 1910							
Broken China	(2)	3.97	3.71	3.84	1.27	1.24	1.25
Ceylon chips	(4)	8.39	5.88	7.15	4.18	0.51	2.32
Broken Batavia	(4)	3.90	3.57	3.78	0.34	0.25	0.29
Year 1911							
Broken China	(14)	3.72	2.78	3.27	1.00	0.50	0.76
Broken Batavia	(7)	5.04	3.57	4.32	0.86	0.21	0.48
Saigon	(6)	4.80	3.71	4.21	0.79	0.43	0.66
Seychelle	(4)	4.80	3.57	4.10	0.61	0.28	0.38

As the table shows, prior to 1909, the quality of broken China imported made it a difficult problem for the spice grinders to conform with the maximum total ash and acid insoluble ash standards of six and two per cent., respectively, given in Circular No. 19, Office of the Secretary of Agriculture, because the bales were often full of pebbles and dirt. However, after the Food Inspection Officials had rejected an importation, broken China changed for the better, and unless very cheap material is bought the spice grinder has very little trouble with this variety today.

Table II shows analyses of samples of other varieties ground in small lots in the laboratory. The flavors of these samples vary from the mild Seychelle cassia to the strong Saigon. The barks with the exception of the Seychelles and Batavias are dark in color, but vary in thickness and shape. The volatile ether extract on which the strength of the flavor is supposed to depend varies remarkably as also does the crude fiber.

Table II.—Percentages.

Variety.	Total ash.	Water soluble ash.	Ash insoluble in HCl.	Volatile ether ext.	Non-volatile ether ext.	Alcohol ext.	Crude fiber
Seychelle bark (a)	4.08	2.54	0.29	0.66	1.87	9.16	49.49
Seychelle bark (b)	5.49	2.73	0.07	0.70	1.99	9.72	44.66
Ordinary broken China	3.96	0.91	1.24	0.90	2.91	3.76	24.84
No. 1 broken Saigon	3.77	1.25	0.05	3.39	4.13	7.80	25.29
Extra No. 1 Batavia	2.92	0.71	0.09	2.45	2.95	9.07	13.33
Pakhoi rolls	2.62	0.82	0.33	1.16	2.58	8.86	21.07
Coarse Corintjie	3.14	1.09	0.48	2.23	3.52	5.24	28.16
Regular No. 1 Corintjie	5.97	2.08	0.13	1.33	4.45	6.78	19.04
China rolls	2.85	0.64	0.15	1.64	3.32	7.14	24.73
Good short stock Batavia	4.10	1.67	0.19	2.49	4.10	9.38	14.08
Kwangsi rolls 3rd	3.39	1.45	0.21	2.71	4.45	6.78	18.61

Table III gives analyses of twelve samples of ground cinnamon purchased in retail packages and representing the general character of the cinnamon offered to the consumer in the eastern market.

These samples are blends of the different varieties, and with a few exceptions comply with the standards of Circular No. 19. It would appear that by using ordinary caution in buying and blending, no difficulty should be experienced in complying with the standards of Circular No. 19 in regard to total and acid insoluble ash. It must be understood that the spice grinder

TABLE III.—PERCENTAGES.

Samples.	Total ash.	Water sol. ash.	Ash in sol. in HCl.	Volatile ether ext.	Non-volatile ether ext.	Alcohol ext.	Crude fiber.
1.	6.90	1.34	2.64	1.44	2.85	10.68	36.88
2.	3.37	0.92	0.90	1.83	3.89	6.28	28.88
3.....	6.88	0.78	2.80	1.68	3.80	6.28	31.14
4.....	9.35	0.86	6.11	1.81	3.40	6.80	29.10
5.....	3.44	1.28	0.43	0.67	1.88	7.76	23.40
6.....	3.50	0.85	1.03	1.58	3.80	8.08	25.06
7.....	3.53	1.19	0.49	0.93	2.01	7.66	24.30
8.....	3.88	1.32	0.31	1.03	2.88	6.74	26.96
9.....	4.75	1.07	1.54	1.40	3.01	7.76	23.34
10.....	2.52	0.09	0.15	0.79	1.92	8.46	27.16
11.....	3.50	1.08	0.45	0.72	1.42	6.04	23.74
12.....	4.15	1.34	0.64	0.63	1.91	7.88	26.49

does not practice blending to work in dirty material, but because blending is necessary to obtain the desired flavor that is demanded by the trade.

LABORATORY WEIKEL & SMITH SPICE CO.,
PHILADELPHIA, PA.

THE RIPENING OF HOPS.

By C. E. BRADLEY AND H. V. TARTAR.

Received April 22, 1912.

The changes which take place in the chemical composition of the hop cone during the ripening period are of interest both from the scientific and from the technical standpoint. Although the composition of the bitter principles of the hop has been known for a long time, their chemical constitution is a perplexing subject which has in recent times engaged the attention of a number of investigators. From their studies, it appears that some of the constituents of the hop cone are closely related in chemical composition, and it is quite possible that changes take place during the ripening period in which one constituent passes over into the form of another. If this does occur, a study of the composition of the hop cone at different stages of ripeness might be valuable in throwing light on the chemical constitution of the different bitter principles.

From the technical standpoint, it is important that hops should be picked at the degree of ripeness when they possess the maximum brewing value. Recent investigations show that the major part of the actual brewing value of hops lies in the content of soft bitter resins, and hence the amount of these constituents in the hop cone at different stages of ripeness is of prime importance. At present, many brewers, regardless of intrinsic value, insist that hops should be picked somewhat green while others prefer to have the cones fully ripened. As a result, the hop growers who desire to produce a product of high quality are at a loss to know just when to gather their crops.

Because of the nature of the literature on the chemical composition of the hop, it may be well to state, by way of explanation, that investigators are agreed that the principal constituents of the hop cone are: a volatile oil, a hard resin commonly designated as the "gamma" resin, two soft bitter resins designated as the "alpha" and "beta" resins, a wax, and a tannin. The constituents designated as resins are not true resins, but owing to the common use of the term in this connection, the authors have continued its use. The recent work of Siller[1] indicates that the gamma resin may be composed of two different substances, but the work is hardly conclusive and we believe needs further study.

EXPERIMENTAL PART.

In August, 1910, a study was begun at this laboratory of the composition of the hop cone at different stages of the ripening period. The samples were gathered approximately five days apart, the first being picked August 11th, the last September 26th, and all taken from the yard of the Seavy Hop Company, near Corvallis, Oregon. In collecting, representative cones of various sizes were taken from the upper and outer portion of the vines, which was well exposed to the sun. On August 11th, two samples were secured, one being of the smaller and the other of the larger and more fully developed cones.

Very soon after the samples were gathered they were spread out and allowed to dry in the shade at room temperature. When the drying operation was complete, the hops were bagged, great care being taken not to crush the cones and to avoid loss of the lupulin through sifting.

In the analytical work, the method of the authors[2] for the determination of the hard, total, and soft (bitter) resins was employed. The separation of the alpha and beta bitter resins was carried out according to the method outlined by Siller.[3] Chapman's[4] method was used for the determination of tannin. Moisture was estimated by drying *in vacuo* over sulfuric acid at room temperature. The determination of the wax was made incident to securing the solutions

COMPOSITION OF HOP CONES AT DIFFERENT STAGES OF THE RIPENING PERIOD.

Sample No.	Date of picking.	Moisture	Dry matter	Composition of Dry Matter (Percentages). Wax.	Total resins.	Total soft bitter resins.	Alpha resin.	Beta resin.	Gamma resin.	Tannin
1	Aug. 11 (cones smaller size).	8.07	91.93	0.52	10.39	8.44	1.88	6.56	1.95	3.48
2	Aug. 11 (cones larger size)..	7.32	92.68	0.57	12.20	10.76	2.74	8.02	1.44	2.92
3	Aug 16.....	7.71	92.29	0.37	14.07	12.56	3.53	9.03	1.51	2.98
4	Aug. 21.....	10.67	89.33	0.55	15.00	13.76	3.84	9.92	1.24	2.59
5	Aug. 26.....	10.12	89.88	0.34	16.24	14.51	3.92	10.59	1.73	2.88
6	Aug. 31.....	9.31	90.69	0.46	16.48	15.17	4.82	10.35	1.31	3.06
7	Sept. 5.....	8.60	91.40	0.35	18.39	16.79	6.27	10.52	1.60	2.81
8	Sept. 11.....	9.42	90.58	0.32	20.48	18.24	7.07	11.17	2.24	3.36
9	Sept. 19.....	8.87	91.13	0.38	20.57	18.41	8.47	9.94	2.16	3.28
10	Sept. 26.....	7.30	92.70	0.33	20.67	19.41	8.40	11.01	1.26	2.76

[1] *Ztg. Untersuch. Nahrung-Genuss.*, **18**, 241.
[2] THIS JOURNAL, **4**, 209 (1912).
[3] *Ztg. Untersuch. Nahrung Genuss.*, **18**, 241.
[4] *J. Inst. Brew.*, **13**, 646 (1907); **15**, 360 (1909).

necessary to the determination of the total resins. The extract obtained from extracting the hops with ether was taken up with alcohol, and the wax, insoluble in this solvent, was collected on a tared filter, washed with alcohol, dried at room temperature and weighed. Owing to the exceedingly small amount of volatile oil present and the consequent difficulty of making a quantitative estimation, the determination of this constituent was omitted.

The results of the analyses are given in the preceding table. In order to afford an accurate comparison, the amounts of wax, tannin, and the different resins have been calculated to dry matter.

The results show that there is a continuous increase in the amount of soft bitter resins throughout the ripening period. The riper the hop, the richer it is in these substances and if high soft bitter resin content is a criterion of brewing value, the fully ripened hop is much to be preferred. The ratio of the amount of alpha bitter resin to the amount of beta bitter resin is of interest. On August 11th, the ratio was 1 : 3.48, while on September 26th, it was 1 : 1.30. Between the first picking and the last, the amount of alpha bitter resin increased 450.5 per cent., while the beta bitter resin increased but 167.8 per cent. There seems to be no marked change during the ripening period in the amount of gamma resin, wax and tannin. From the analytical data, there is also no evidence that one constituent changes to the form of another during the process of ripening.

AGRICULTURAL EXPERIMENT STATION,
CORVALLIS, OREGON.

ANALYSES OF SOME FATS OF THE AMERICAN BUFFALO (BISON).

By ALBERT H. SCHMIDT.

Received March 1, 1912.

During the month of December, 1905, there was sold in the Union Stock Yards a mixed car lot of stock, consisting of some cattle, a few so-called Cattaloes—a cross between cattle and buffalo—and one pure bred specimen of the buffalo, or American bison. I obtained five different kinds of the fats of this particular animal and analyzed them.

Having gone over all the available literature on fats and oils and found no reference to previous analyses of buffalo fats, I believe it may be of interest to place on record the analyses of various fats of an animal that is now almost extinct on our continent.

For comparison, I also obtained samples of the corresponding fats from a lot of native steers ranging in age from two to four years. These fats as well as the buffalo fats were rendered in the laboratory.

The one striking point is the difference in the kidney fats of the cattle as compared with the buffalo. This is no doubt due to the difference in size of the kidneys of the buffalo, as compared with cattle. The buffalo kidney is about one-half the size of the cattle kidney and is surrounded by a compact and comparatively small amount of fatty tissue, whereas the cattle kidney is large, and in native cattle is surrounded by a large mass of fatty tissue which is much softer and less

ANALYSES OF BUFFALO FATS.

Name of fat.	Sp. gr. at 15°.	Free fatty acids.	Titer.	Iodine No.[1]	Saponification No.
Caul fat	0.9263	0.90%	50.1° C.	33.23	200.6
Kidney fat	0.9346	1.65%	52.2° C.	29.45	199.3
Ruffle fat	0.9364	1.90%	51.0° C.	32.50	199.4
Paunch fat	0.9244	1.50%	47.4° C.	34.92	204.2
Chip fat	0.9344	1.25%	49.6° C.	35.16	199.5

ANALYSES OF FATS OF NATIVE STEERS, TWO TO FOUR YEARS OLD.

Name of fat.	Sp. gr. at 15°.	Free fatty acids.	Titer.	Iodine No.[1]	Saponification No.
Caul fat	0.937	0.30%	48.8° C.	36.10	203.0
Kidney fat	0.933	0.60%	42.85° C.	48.86	196.0
Ruffle fat	0.932	0.25%	48.6° C.	36.13	199.0
Paunch fat	0.934	0.20%	43.8° C.	46.04	201.3
Chip fat	0.937	0.25%	43.4° C.	47.20	196.8

firm than the fatty tissue of this particular buffalo.

This anatomical difference in size of the buffalo kidney as compared with its close relative, the cattle, is not readily explained. In its wild state the buffalo was often without water for three or four days when roaming over our semi-arid plains. What bearing this may have on the size of the kidneys of animals living under such conditions is open to question.

The hindquarters of the buffalo are far lighter than those of cattle and, therefore, it is logical to assume that the organs in the posterior part of the buffalo would be smaller than the corresponding organs of cattle.

I am not able to account for the high percentage of free fatty acid in the buffalo fats, as they were rendered when comparatively fresh and in the same manner as the cattle fats. I had no record of the age of this buffalo bull at the time of slaughter, but was told that it was about seven or eight years old.

LABORATORY OF SULZBERGER & SONS COMPANY,
CHICAGO.

THE DETERMINATION OF EUCALYPTOL (CINEOL) IN ESSENTIAL OILS.[2]

By FRANCIS D. DODGE.

Received May 15, 1912.

The methods so far suggested for the determination of eucalyptol in essential oils have proved rather unsatisfactory, for, although eucalyptol possesses to an unusual degree the capacity of forming molecular compounds with a variety of other substances, these compounds are not, in general, easily purified, nor stable enough to be utilized for analytical purposes.

The hydrochloride, hydrobromide, phosphate, arsenate, oxalate and ferrocyanide have been described, as well as the compounds with iodol beta-naphthol, and resorcinol, but the attempts to make any of these the basis of an assay method have not been very successful. After much fruitless experiment along this line, I was compelled to abandon the compounds of eucalyptol, and endeavored to utilize another property, namely, its stability to cold permanganate solution.

Eucalyptol, being a saturated cyclic compound, of considerable stability to alkaline reagents, is practi-

[1] Iodine numbers determined by Wijs' method.

[2] Read before N. Y. Sec. Am. Chem. Soc., April 8, 1910.

cally unaffected by cold permanganate, whereas all terpenes and unsaturated compounds are oxidized, more or less readily, to soluble products.

The unattacked eucalyptol can be measured, and its purity confirmed by physical tests.

The assay may be conducted as follows: 10 cc. of the oil (eucalyptus or cajeput) are run into a 500 cc. flask having a narrow neck, and 5–6 per cent. $KMnO_4$ solution added in small portions, with shaking, keeping the flask in ice water, until the reagent is no longer reduced. The amount required will vary from 100 cc. for rich oils to 400 cc. for inferior ones. When an excess of permanganate has been added, the flask is kept cold, with occasional shaking, for 12–18 hours. The precipitated manganic oxide is then dissolved by sufficient sulphurous acid (or sodium bisulphite and hydrochloric acid) and the flask filled with water, allowing the unoxidized oil to collect in the neck. After settling, the oil is transferred by a capillary pipette, to a graduated tube, washed with a little alkali to remove traces of sulphurous acid, and the volume read off.

All reagents should be perfectly clear, or filtered if necessary.

The eucalyptol thus obtained should show:

Sp. gr. at 15°, 0.929–0.930.

Opt. rotation, ±0°.

Soluble in $3^1/_2$ volumes 60 per cent. alcohol at 25°.

This method has been used for several years with very satisfactory results. Examples:

	S. G.	O. R.	Per cent. E. by vol.	S. G. of E.
Oil eucalyptus.....	0.928 @ 15°	+0.05°	85	0.929
	0.923 @ 15°	+0.55°	81	0.929
	0.915 @ 15°	—3.15°	52	0.929
	0.908 @ 25°	+0.50°	68	0.929
	0.905 @ 25°	—6.0°	66	0.930
	0.098 @ 25°	—4.16°	74	0.928
Oil cajeput.....	0.913 @ 25°	—2.10°	60	0.929
	0.916 @ 25°	—1.45°	61	0.927
	0.914	—1.96°	56	

Check assays on known mixtures of eucalyptol, terpenes, and terpineol, have shown the reliability of the method for technical work.

The isolation of the eucalyptol in a pure state is a great advantage, as any stable compounds which might be present are immediately manifested by their effect on the physical constants. Thus:

+ Camphor (stable to $KMnO_4$) increases S. G. and shows + O. R.

Inactive camphor (stable to $KMnO_4$) increases S. G.

Fenchone (stable to $KMnO_4$) increases S. G. and shows + O. R.

Paraffins or petroleum products increased, diminish S. G. and solubility.

Borneol (oxidized to camphor).

Menthol (oxidized to menthone).

Menthone (slowly oxidized) diminishes S. G. and shows O. R.

Bornyl acetate (stable) increases S. G. and shows O. R.

The method as outlined is, I believe, the only direct method among those applicable to constituents of the essential oils, *i. e.*, one in which the compound to be estimated is isolated in a pure and determinable shape.

LABORATORY DODGE & OLCOTT CO.,
BAYONNE, N. J.

RECENT ANALYSES OF THE SARATOGA MINERAL WATERS.

By LESLIE RUSSELL MILFORD.

Received February 21, 1912.

GENERAL.

This group of mineral springs is recognized as one of New York State's unique natural resources, and their discovery dates back to 1767 when, according to tradition, the Indians brought Sir William Johnson to the High Rock Spring to be treated for gout.

The general belief is that the wells and springs in this region have a common source far down in the earth and situated along a geological fault, the strata at the west being many feet above those corresponding in the east.

The minerals are held in solution by the great amount of carbon dioxide which saturates the waters along the mineral stratum. This stratum is supposed to be the remains of an extinct volcano or the remnant of a Silurian Ocean. It was through this geological fault that the springs found their way to the surface flowing by their own gas pressure.

The popularity of these springs soon became known, and a water resort of great therapeutic value, resembling, in quality, the famous French Vichy, was given to the public.

The springs and wells at Saratoga may be divided into three groups: Geysers Park, Congress Park, and High Rock Park, each of which contains its supply of mineral waters.

About fifteen years ago it was discovered that the carbon dioxide with which these mineral waters were charged could be profitably separated from the waters and sold. A large industry soon became established in Saratoga, companies being formed, generally called "gas companies," for the promotion of the industry. At first these gas companies extracted the carbon dioxide from what were called "dry wells" or "pockets" and also from the mineral water as it naturally issued from the ground. But later it was discovered that by pumping with more powerful and modern machinery a far larger amount of mineral water could be forced from the ground and consequently more gas extracted.

This pumping soon began to have a marked effect on the other springs, causing a diminution in flow and alteration of the minerals in solution. A great amount of litigation was soon begun between the spring owners and the gas companies, the spring owners showing that pumping affected the flow of their springs and the "gas companies" asserting a property in the flow of the mineral waters from the springs on or under their lands. The result of this agitation over the effect of pumping caused an "anti-pumping law" to be passed by the legislature in 1908. The passage of this act was followed by more lawsuits extending over a period of many months. The need of unified ownership in the springs became apparent

and the legislature in 1909 passed an act appointing the Commissioners of the State Reservation at Saratoga Springs, who at once began their duties of preserving the springs and restoring them to their former natural condition.

To aid them in their work special investigations were undertaken by the Division of Laboratories of the State Department of Health at the request of the Saratoga Reservation Commission.

The analyses, and their explanations which follow, represent the work which has been recently completed and a part of the series of the analyses which are to be made.

The writer personally collected and sealed the samples in 5-gallon demijohns so that the analyses are known to be from true samples of the mineral water as it came from the source.

An important feature to note with this work is that the State Hygienic Laboratory is only forty miles from the Reservation at Saratoga so that a great amount of field work was easily carried on in connection with the laboratory examinations. Also a quick

	Constituents as Actually Determined.					Hathorn Spring No. 2.	Hathorn Spring No. 3.
	Hathorn Spring No. 1			Coesa (Carlsbad) Spring.			
	1.	2.	3.	4.	5.	6.	7.	8.
Formula.	Results in milligrams per liter							
SiO_2	21.58	19.60	13.85	8.60	13.50	7.70	8.15	8.50
SO_4	trace	5.60	21.42	3.77	2.80	27.00	12.60	6.60
HCO_3	4354.14	3585.60	2219.00	4746.34	4244.50	3912.50	5677.90	5581.60
NO_3	*a*	none	none	*a*	none	none	none	trace
NO_2	*a*	none	trace	*a*	none	none	none	none
PO_4	0.05	none	none	*a*	none	none	none	none
AsO_4	*a*	none	none	*a*	none	none	none	none
BO_3	trace	small amount	trace	trace	small amount	trace	trace	trace
Cl	5370.03	3685.50	2293.00	5150.45	4419.60	4180.00	7044.75	5775.70
Br	20.31	26.90	2.05	*a*	40.30	40.90	29.84	16.10
I	2.82	1.50	0.60	*a*	1.60	1.90	3.81	1.26
Fe	5.95	*a*	18.70	10.08	*a*	16.10	4.50	14.30
Fe and Al	7.14	9.80	19.40	*a*	13.10	16.90	16.30	17.30
Al_2O_3	2.24	*a*	1.40	*a*	*a*	1.50	8.50	7.60
Mn	*a*	*a*	none	*a*	*a*	3.60	trace	none
Ca	1008.71	650.70	499.80	733.65	628.60	781.90	974.85	1057.80
Mg	826.73	228.80	90.00	332.90	298.80	288.40	472.40	412.30
Ba	17.54	5.50	12.31	15.93	10.10	4.70	25.30	13.70
Sr	trace	trace	trace	trace	trace	1.70	6.10	2.70
K	85.90	197.20	471.40	304.53	237.80	242.20	442.80	365.50
Na	3455.29	2430.70	1280.10	3525.55	3014.50	2556.90	4369.00	3621.90
Li	20.16	0.50	3.70	15.18	5.30	12.20	11.60	12.80
NH_4	*a*	10.70	6.00	*a*	13.40	5.53	18.10	13.30
Oxygen to form Fe_2O_3					5.70			
F	trace							
	Hypothetical Form of Combination.							
NH_4Cl	*a*	31.80	17.90	*a*	39.67	16.46	53.90	39.60
LiCl	*b* 150.28	3.00	22.40	*b* 113.89	31.80	74.20	70.50	76.10
KCl	164.11	350.70	898.80	574.05	415.60	422.10	815.60	676.40
NaCl	8720.45	5762.40	3253.80	8324.11	6873.50	6444.70	10825.90	8957.30
KBr	*c* 20.36	40.00	3.00	*a*	60.00	60.00	43.75	25.00
KI	*d* 2.02	1.90	0.40	*a*	2.10	2.50	5.00	1.65
Na_2SO_4	*e* trace	8.20	31.70	*e* 5.47	4.10	39.90	18.64	9.80
$NaNO_3$	*a*	none	none	*a*	none	none	none	trace
$NaNO_2$	*a*	none	trace	*a*	none	none	none	trace
$NaBO_2$	trace	trace	trace	trace	trace	trace	trace	trace
$NaHCO_3$	73.32	586.40	276.10	898.61	1126.70	68.19	362.10	331.80
$Ba(HCO_3)_2$	29.70	10.40	23.30	30.10	19.10	8.90	47.80	25.90
$Sr(HCO_3)_2$	trace	trace	trace	trace	trace	4.00	14.60	6.40
$Mg(HCO_3)_2$	3017.52	1377.80	556.40	2020.71	1798.90	1750.70	2867.40	2502.60
$Ca(HCO_3)_2$	2918.05	2635.30	2024.20	2971.30	2545.80	3166.70	3948.10	4281.40
$Fe(HCO_3)_2$	19.29	31.10	29.60	32.15	*a*	25.50	37.70	22.50
MnO_4	*a*	none	none	*a*	*a*	5.00	trace	none
Al_2O_3	1.24	*a*	1.40	*a*	18.80	1.50	8.50	7.60
Fe_2O_3								
SiO_2	21.55	19.60	13.85	8.60	13.50	7.70	8.15	8.50
Total solids	15154.82	10858.60	6152.85	14978.99	12949.70	12098.05	18764.59	16640.75
Residue on evaporation	12663.61	*a*	6030.00	*a*	*a*	10570.00	16220.00	13830.00
Temperature	*a*	*a*	10.5° C.	*a*	*a*	11° C.	10.5° C.	10.4° C.
Organic matter	trace							
Density	1.0115							
NaBr	26.23							
NaI	2.39							
NaF	trace							
Na_3PO_4	0.10							
K_2SO_4	trace			6.84				
$LiHCO_3$	194.74			147.40				

a, Not given
b, Equivalent of $LiHCO_3$ reported.
c, Equivalent of NaBr reported.
d, Equivalent of NaI reported.
e, Equivalent of K_2SO_4 reported.

1, C. F. Chandler, *The American Chemist*, **2**, No. 6, (1871).
2 and 5, "Mineral Waters of the U. S.," Dept. of Agriculture, *Bulletin* No. **91.**
3, 6, 7 and 8, Files of New York State Department of Health, January, 1912.
4, Analysis by E. E. Smith, Ph.D., M.D., August, 1901.

delivery of the samples for mineral analysis is to be had.

The methods given in *Bulletin* **91,** Bureau of Chemistry,[1] except for the determination of lithium, were followed. For lithium a new method was adopted which is described by the author in another paper.

The waters of the Hathorn Spring No. 1 and the Coesa Spring (formerly known as the Carlsbad) have been analyzed by other chemists and the results of the analyses have been published in the literature, but for the sake of comparison these older analyses have been inserted beside the new ones. Where the results have been combined in a different way than was adopted by the Bureau of Chemistry and followed by the New York State Department of Health, the writer has computed them to a comparable equivalent. The hypothetical forms of combination have been computed as milligrams per liter.

From the data we can see that great changes have taken place in the springs from time to time. The water of the Hathorn Spring No. 1 when analyzed by Prof. Chandler forty years ago was over twice as strongly mineralized as it is now. It was also less mineralized when the sample was taken last July than it was when analyzed by the Bureau of Chemistry of the U. S. Department of Agriculture.

The water of the Coesa Spring contained less minerals in solution when the sample was taken in November, 1911, than it did when analyzed by Dr. Smith or the U. S. Department of Agriculture.

The amount of lithium found in the last analyses is higher than that reported in the results published in *Bulletin* **91,** because of a new method employed which now gives more complete results.

The Hathorn Spring No. 1 is situated in the village of Saratoga, while the Coesa is situated at the Geysers.

These two waters have an abundant supply of gas and are suitably mineralized.

The Hathorn Spring No. 2 and Hathorn Spring No. 3 have never been analyzed by other analysts, so that no data for comparison are available. These two springs are situated in the Geysers district about 300 feet apart and were found in the early part of 1910 by drilling. Hathorn No. 2 is the most highly mineralized spring in Saratoga and its waters are pronounced by eminent physicians to be of great therapeutic value. Hathorn No. 3 is of the same general nature as Hathorn No. 2. As seen from the analyses these springs contain the important constituents—magnesium, sodium, lithium and carbon dioxide.

ANALYSES OF THE GAS.

The supply of carbon dioxide being great, it was thought advisable to analyze the gas from some of the important springs where the sample could be easily collected.

SARATOGA SPRING WATERS.

The gas was collected in a five gallon demijohn by first filling it with the charged water, issuing from the spring, then inverting and displacing the water by the gas from the spring. The apparatus of Hempel was used for measuring the sample, then it was estimated by the ordinary absorbents in the absorption pipettes.[1] Hydrogen sulphide was determined by passing the gas through a measured amount of standard arsenious acid solution and titrating back with iodine, using starch as an indicator.[2]

GAS FROM COESA (CARLSBAD) SPRING.

Sample of gas taken July 14, 1911:		
Sample for analysis corrected	100 cc.	
Carbon dioxide	97.5	
Oxygen	0.0	
Combustible	0.0	
Nitrogen and non combustible	2.5	
Hydrogen sulphide	0.0	When three liters of the gas were tested.

GAS FROM HATHORN SPRING NO. 3.

Sample of gas taken July 13, 1911:		
Sample for analysis corrected	100 cc.	
Carbon dioxide	98.1	
Oxygen	0.0	
Combustible	0.0	
Nitrogen and non-combustible	1.90	
Hydrogen sulphide	0.0	When three liters of the gas were tested.

No samples of gas were taken from Hathorn Springs Nos. 1 and 2.

BACTERIOLOGICAL EXAMINATIONS.

The waters of these springs have been examined bacteriologically from time to time, and the results showed at the time these samples were taken that the bacterial count was very low; no organism of the *B. coli* type was isolated. This proves that the springs are of a high sanitary purity.

In the near future other analyses will be made, and the results will be published from time to time.

The writer wishes to express his gratitude to the State Department of Health and the Saratoga Reservation Commission for the permission to use their data and information.

STATE HYGIENIC LABORATORY,
STATE DEPARTMENT OF HEALTH,
ALBANY, N. Y.

[1] "Mineral Waters of the United States," U. S. Dept. of Agriculture, Bureau of Chemistry, *Bulletin* **91,** 1907.

DETERMINATION OF LITHIUM.

By LESLIE RUSSELL MILFORD.

Received February 21, 1912.

In the work with the first samples of the Saratoga mineral waters, which the writer has been analyzing, the determination of lithium was found to be difficult and the results obtained were not satisfactory because of the fact that parallel determinations would not check and too small volumes of water had to be used.

The waters of these springs are highly mineralized, the chlorides ranging from 100 to 11,000 parts per million. Therefore, a great deal of trouble was experienced in volatilizing the ammonium salts when working with large volumes of water. Mechanical loss, due to decrepitation and splitting apart of the crystals, was a constant source of error. On the other hand, if one took a small volume of water the chlorides could be dried and the ammonium salts driven off more easily, but the possibility of multiplying errors would be great because of the relative small amounts of lithium present.

The need of an improvement or change of the method given on page 29, *Bulletin* **91,** of the Bureau of

[1] Hempel-Dennis, "Methods of Gas Analysis," 1906.

[2] Sutton, "Volumetric Analysis" (Mohr's method), 1901.

Chemistry became apparent. By consulting the literature and various solubility tables[2] and studying the methods of Gooch,[3] Treadwell,[4] Kennicut,[5] Frenkel,[6] and Rammelsberg,[7] the following procedure was adopted whereby a larger volume of water could be used and a residue obtained which would give, when treated, a lithium salt containing only a spectroscopic trace of sodium and potassium.

Method.—Two hundred to five hundred cc. of the water are evaporated to dryness in a large platinum dish with the occasional addition of small amounts of concentrated hydrochloric acid. After all of the water has been evaporated to dryness the dish and contents are heated at 120° C. for about 30 minutes to dehydrate the silica. The residue is then treated with a little dilute hydrochloric acid, just enough to moisten the contents of the dish. Then about 25 cc. of 95 per cent. alcohol are added and the residue is rubbed up with a small pestle until all lumps and crystals are crushed. The alcoholic extract is then poured on an 11 cm. quantitative filter and the filtrate caught in another platinum dish. The residue is washed with 95 per cent. alcohol until it shows no lithium line when examined in the spectroscope. The alcoholic filtrate and washings are united and evaporated on the water bath. When all of the alcohol has evaporated some dilute hydrochloric acid is added to the contents of the dish, and the whole evaporated to dryness and then the residue rubbed up with absolute instead of 95 per cent. alcohol. The filtrate is caught as before in a platinum dish and the residue on the filtrate washed with absolute alcohol until no lithium line is seen when tested from time to time with the spectroscope. The alcohol is evaporated and the dry residue taken up with a little dilute hydrochloric acid. Calcium hydrate is added until the solution is alkaline. The magnesium is precipitated as the hydrate and the solution is filtered. To the filtrate add ammonium hydrate and ammonium oxalate to precipitate the calcium. This is allowed to stand twelve hours or over night when it is filtered off. The calcium oxalate precipitate must be thoroughly washed (usually about 100 cc. of water is sufficient) as lithium is held relatively fast by the precipitate and does not wash out easily. When the residue no longer shows lithium, as verified by the spectroscope, the solution is evaporated to dryness and the excess of ammonium salts driven off by first heating the dish on a radiator, then over the free flame. The residue in the dish is taken up with a little dilute hydrochloric acid, heated and ammonia and ammonium oxalate are again added to precipitate any calcium which might be present. In any case the solution is filtered from any calcium or magnesium that precipitates on concentrating the solution. The filtrate is evaporated to dryness and all ammonium salts are driven off by heating in platinum to a little below redness. The residue is again taken up with water, filtered, and washed (using as little wash water as possible), then evaporated to dryness and heated in platinum to a little below redness to drive off any ammonium salts. All of the calcium and practically all the magnesium have now been removed, and there is left a residue containing lithium chloride with traces of sodium and potassium chlorides. If we have iodides and bromides present, this residue will contain small amounts of these substances because they are more soluble than the chlorides. In order to insure a residue consisting of chlorides only we treat the contents of the dish with a little dilute hydrochloric acid and chlorine water, evaporate to dryness, and gently ignite. By this we have replaced the iodine and bromine with chlorine.

The residue is now taken up with a little water and treated with a few drops of dilute hydrochloric acid and transferred to a large platinum dish.

About 30 cc. of amyl alcohol are added and the contents of the dish brought to boiling with constant rapid stirring when heating to minimize the bumping caused by the escape of the water. When all of the water has evaporated, the dish is placed on the steam bath and a drop of dilute hydrochloric acid added to reconvert small amounts of lithium hydrate to the chloride. The evaporation is continued until the volume reaches about 15 cc. The amyl alcohol is then filtered into a platinum dish and evaporated to dryness. Water and a few drops of dilute sulphuric acid are now added and the contents of the dish again evaporated to dryness. The excess of sulfuric acid is removed by heating the dish over a radiator and then over the direct flame to dull redness. The dish is cooled, the contents dissolved in water and a few drops of ammonium hydrate are added to precipitate the last trace of magnesium which is invariably present at this stage. Filter, wash with boiling water, evaporate to dryness, free from ammonium salts, and repeat previous process till no more magnesium precipitates on addition of ammonium hydrate. Finally filter into a weighed platinum dish, evaporate to dryness, burn, cool in a desiccator, and weigh as lithium sulfate. From this result we subtract 0.0017 gram to correct for the solubility of the sodium and potassium chlorides in amyl alcohol, their presence having been verified by the spectroscope.

The contents of the filters containing the NaCl, KCl, etc., which were taken out by the 95 per cent. alcohol and absolute alcohol together with the contents of the platinum dish and filter from which the amyl alcohol has been driven off, are all dissolved in water, united, freed from other salts and made up to a definite volume. By using aliquot portions we can determine sodium and potassium by Gooch's method. Or the usual procedure, using a small portion of the silica filtrate, can be followed.

Advantages Given by this Modification: (1) Waters high in chlorides can be handled with ease with no danger of loss of lithium by decrepitation.

[1] and [3] "Mineral Waters of the United States," U. S. Dept. of Agriculture, Bureau of Chemistry, *Bulletin* **91**, 1906.

[2] Atherton Seidell, "Solubilities of Inorganic and Organic Substances," 1907.

[4] and [7] Treadwell-Hall, "Analytical Chemistry," 1911.

[5] Chamot-Redfield. "Analysis of Water for Household and Municipal Purposes," 1911.

[6] M. Frenkel, D.Sc., "Extract from the Records of Medical Hydrology and Climatology," Paris, Dec., 1903.

(2) Large volumes of water can be used, thus reducing the error when computing to milligrams per liter.

(3) The results can be found to check and can be obtained much more quickly by having a residue free from an excess of sodium and potassium chlorides.

(4) The method involves the use of calcium hydrate instead of barium hydrate for the precipitation of magnesium. This procedure does not introduce another substance which has to be removed by ammonia and ammonium oxalate because we have our calcium in common and have a precipitate of calcium oxalate which is less soluble and more easily washed than barium oxalate.

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A NEW VOLUMETRIC METHOD FOR TIN.

By WILLBUR W. PATRICK AND G. C. WILSNACK.

Numerous methods for the determination of tin have been tried out in this laboratory with various degrees of success. Gravimetric methods giving results of the required accuracy are too lengthy and tedious for ordinary use in laboratories where it is required to complete a large number of determinations in a short time. Shorter schemes, such as weighing the combined oxides of antimony and tin, determining antimony in a separate sample, and calculating tin by difference, cannot be used for alloys containing lead, copper, or numerous other metals which are to be found in some commercial alloys, unless the amount of these impurities contaminating the oxides be determined and taken into consideration.

The volumetric methods proved to be rather unsatisfactory, especially if the titrating solution was standardized against a standard reducing solution in preference to C. P. tin. The authors found that determinations on quantities as small as 5% were unreliable, and that on high percentages it was almost impossible to obtain consistently accurate results even if the oxidizing solution was standardized against an equivalent amount of metal treated in an exactly similar manner.

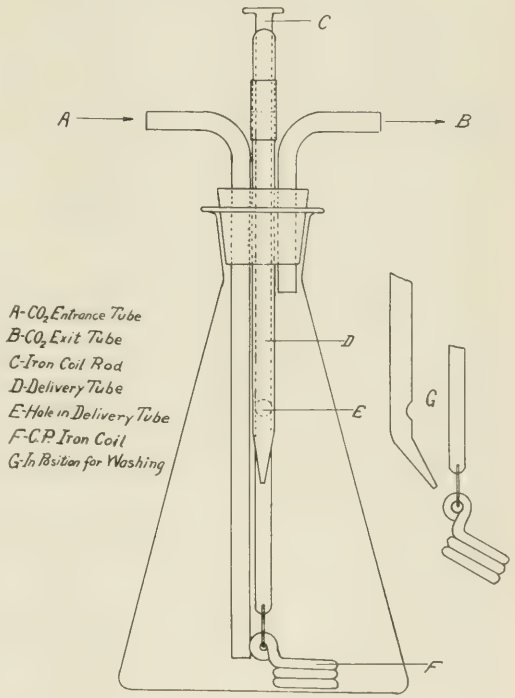
Endeavoring to overcome these difficulties, the following method was finally adopted. The results obtained are consistent and correct to within 0.2 per cent. on amounts of 50 per cent. or over and considerably more accurate on smaller percentages. As large percentages of copper, lead, nickel, and perhaps other metals not experimented with, interfere, it has been found expedient to modify the method somewhat in the presence of these elements. Both determinations will be described.

REGULAR METHOD.

The following scheme of analysis is available where no more than 5 per cent. of either lead or copper is present in the alloy. Where the percentages of these elements exceed this limit a modification of the method is necessary.

Place an amount of sample corresponding to 0.5 gram or less of tin in a 500 cc. Jena Erlenmeyer flask and add 0.15 gram C. P. metallic antimony if as much or more is not already present in the alloy. If the sample contains less than this amount it is necessary to make up the deficiency. Add 10 cc. of concentrated sulphuric acid and heat to effect solution. Remove from the hot plate and cool. Dilute the cold sulphuric acid solution with 10 cc. of water, add 60 cc. of concentrated hydrochloric acid, and then 40 cc. more of water. Prepare a four-hole rubber stopper that fits the neck of the flask. Through one hole pass a glass tube bent at right angles reaching to the bottom of the flask and through the hole diagonally opposite insert another tube bent in a similar manner but extending only a short distance below the bottom of the stopper. Through the third hole pass a long thin glass rod fitted with a 2″ piece of platinum wire. This rod should fit rather snugly without, however, giving any difficulty to the operator in raising or lowering it during the determination. The platinum wire is now bent into the shape of a hook and a piece of very nearly C. P. iron wire attached. Swedish iron in plates of $^1/_8$″ thickness cut into strips of $^1/_8$″ in width and four inches in length, curled up in the form of a spiral, will suit the purpose well. Through the fourth hole pass a $^1/_2$″ tube 4″ long and drawn out at the lower end to an opening small enough to enable the operator to introduce iodine solution in sufficiently small quantities to obtain the starch iodide reaction within one drop of titrating solution. The tapered end is bent slightly in the di-

Volumetric Tin Apparatus



rection of the submerged wire for the purpose of conducting a stream of water to free the iron from adhering tin solution after it has been withdrawn from the liquid. This delivery tube should also be provided with a $^1/_4$" hole about $^3/_4$" above the lower opening to afford a means of escape for the carbon dioxide gas which is being rapidly introduced during the titration. A carbon dioxide generator is connected to the long tube while a piece of rubber tubing connects the short tube opposite to a 100 cc. pipette which dips into a reservoir of water. This automatically prevents any air from entering the system when a partial vacuum is formed in the flask during the determination, which cannot be taken care of by the entering carbon dioxide gas. Having attached the iron to the platinum wire, the rubber stopper is firmly placed in position in the neck of the flask and the rod lowered so that the spiral of wire rests on the bottom of the flask. The generator and water seal are attached as previously described, a cap is placed over the opening of the large delivery tube and a rapid stream of carbon dioxide gas passed through the system. After a few minutes it may safely be assumed that all of the air is expelled from the flask, whereupon heat is applied and the contents permitted to boil for 25 minutes. The solution when first placed in the flask appears a deep yellow or orange, depending, of course, upon the constituents present, but shortly before commencing to boil it becomes colorless and finally black, due to the liberated metallic antimony. After the reduction is complete, remove the burner, plunge the flask into a large container of cold water and allow to remain until thoroughly cold. The iron wire is then raised to a position directly below the end of the delivery tube. The cap of this tube is then removed and with all possible haste a stream of cold *freshly boiled* water permitted to play upon the spiral to free it from any adhering tin solution, after which the wire is raised so that the titrating solution will not come in contact with it. Freshly prepared starch is added and, without interrupting the passage of gas, standard iodine solution introduced into the flask as fast as the burette will permit. When near the end point, which is indicated by the reluctant disappearance of the blue, the titration can be carried on very slowly until completed. The blue of the starch iodide is not permanent, disappearing after a minute or two, which fact does not, however, detract from the accuracy of the determination.

It is not to be understood that the tin is completely reduced by the direct action of the iron alone, neither will the addition of pulverized metallic antimony bring about the desired result. However, this metal as deposited is in a state where its chemical activity is at a maximum, thus enabling it to fully complete the reduction.

Standardize the sodium thiosulphate, which serves to determine the strength of the iodine solution, very carefully against a bichromate or permanganate solution of known strength. It is essential that the utmost accuracy be employed in the above standardization, since 0.1 cc. more or less of a $N/10$ oxidizing solution makes a considerable difference in the ultimate tin value of the iodine. It has been found advisable in finding the normality of a freshly prepared iodine solution to check the theoretical standardization against C. P. tin.

MODIFIED METHOD.

A modified method is used when 5 per cent. or more of copper or lead, or any other interfering element, is present in the specimen to be analyzed.

Place 0.5 to 1 gram of sample in a small casserole and add if necessary 0.15 gram of antimony as in the regular method. Cover the sample with 8–10 cc. of concentrated nitric acid and evaporate to dryness. It is advisable in order to facilitate the subsequent filtration to bake strongly for about 15 minutes. Cool and add 20 cc. of 1–1 nitric acid, and, after breaking up the lumps with a stirring rod, filter and wash several times with hot water. If the baking has been conducted properly no traces of oxides will be discernible in the filtrate. The precipitate with the filter paper is then placed in a 500 cc. Jena Erlenmeyer flask and treated with 20 cc. of concentrated sulphuric acid and 2 grams of potassium sulphate. Place the flask on a piece of asbestos over a medium hot burner and heat carefully till the first violent reaction is over, after which the heat can be increased. Towards the end of the oxidizing operation, while the liquid is still black however from the free carbon present, the flask and contents should be cooled and the sides of the container washed down with a stream of water. The particles adhering so firmly to the wall of the flask that the water does not loosen them should be brought back into the main solution with the aid of a "policeman." The removal of the carbon should by no means be hastened by the addition of an oxidizing agent, since this will cause the antimony to assume the pentavalent form, which must be avoided. The addition of the water will now have a tendency to again cause frothing when the heat is applied, making it necessary to conduct this operation very carefully. From 2–$2^1/_2$ hours are usually required, depending upon the intensity of heat employed, to rid the solution completely of the carbon. Cool, introduce the required amount of water, but add only 45 cc. of hydrochloric acid instead of 60 cc. as in the regular method.

If very large percentages of antimony are present, enough to obscure the end point obtained with the starch solution, it is well to treat in the usual manner up to the point where the metallic antimony separates out. The solution should then be rapidly cooled, filtered with suction and washed with hot water. About 0.10 gram of metallic antimony, which has previously been dissolved in a few cc. of sulphuric acid, is then added, the solution returned to the original container, and the reduction continued. The concentration of the solution after this operation should not be changed to any great extent, the additional acid introduced off-setting in a large measure the water used for washing. Antimony present up to 25 per cent. will not obscure the end point, provided a good light and white background are available.

The accompanying table gives a few results obtained on mixtures containing various amounts of copper, lead and nickel as noted. These figures are fairly representative of the results which may be obtained by the methods described in the preceding pages.

	Approximate amount.					
Method.	Copper. Gram.	Lead. Gram.	Nickel. Gram.	Tin taken. Gram.	Tin found. Gram.	Error. Mg.
Regular.....	..	..	..	0.4040	0.4038	0.2
Regular.....	..	..	..	0.0568	0.0575	0.7
Regular.....	0.03	..	..	0.4470	0.4478	0.8
Regular.....	0.05	0.05	..	0.1143	0.1153	1.0
Modified.....	0.25	0.30	..	0.4060	0.4065	0.5
Modified.....	0.03	0.66	0.03	0.1764	0.1763	0.1
Modified.....	..	0.30	0.05	0.4272	0.4261	1.1
Modified.....	0.15	0.80	..	0.0216	0.0214	0.2
Modified.....	0.08	0.80	..	0.1000	0.1000	0.0
Modified.....	0.50	..	..	0.4530	0.4526	0.4

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A NEW APPARATUS FOR THE VOLUMETRIC DETERMINATION OF CARBON DIOXIDE.

By HOWARD W. BRUBAKER.

Received April 13, 1912.

In THIS JOURNAL for March, 1912, appeared an account, by L. T. Bowser, of a volumetric method for the determination of carbon dioxide. In this method the carbon dioxide is liberated and then absorbed in a solution of potassium hydroxide. This solution is washed into a 100 cc. graduated flask, water added to the mark and an aliquot titrated, using phenolphthalein as the indicator to the disappearance of the red color, then methyl orange, the second part of the titration indicating the amount of carbon dioxide in the solution.

The writer had occasion to try out the method to see whether it could be used by a class of comparatively inexperienced students of chemistry. As a result of a little experience with the method some objectionable features were found with the apparatus used by Mr. Bowser which make it impracticable for use by students. Probably the most objectionable feature is the necessity of washing out the potassium hydroxide from the tall absorbing cylinder into a measuring flask. This process requires skilled manipulation, especially since it is necessary to wash the cylinder thoroughly and yet keep the whole volume of liquid and wash water down to 100 cc., which seems advisable, in order that a sufficiently large fractional portion of the solution may be titrated without using a very large volume.

Another objection lies in the fact that at the end of the decomposition of the carbonate when an attempt is made to distil over some of the liquid, in order to drive the last portion of carbon dioxide into the absorbing cylinder, there is a tendency for the potassium hydroxide solution to suck back into the condensing apparatus. In order to overcome these objections and to make the method applicable for the use of inexperienced students the writer devised the apparatus shown in the accompanying figure.

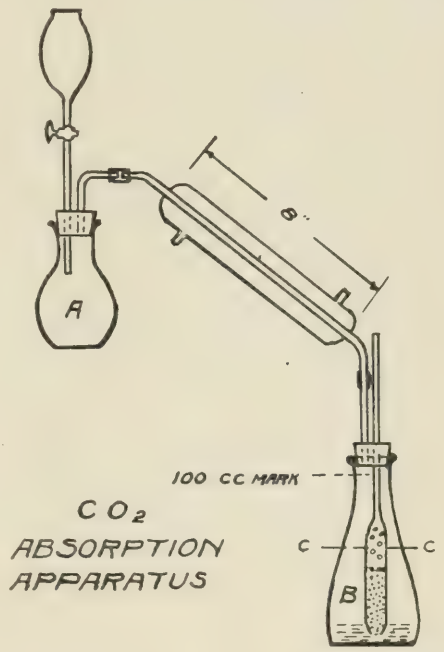
B is a standardized Erlenmeyer flask holding 100 cc. when filled to the mark.

C is a 10 cc. pipette half filled with glass beads, having a coil of copper wire at the bottom to prevent any of the beads from becoming wedged into the tapering part of the tube.

Eight cc. of the potassium hydroxide solution (50 grams KOH in 100 cc. water) are placed in the flask B which is then connected with the condenser as shown in the figure.

One gram of the material to be analyzed is placed in the flask A with about 50 cc. of water. The hydrochloric acid is run in from the funnel, drop by drop, until sufficient has been added to decompose the sample.

The carbon dioxide distils into the flask B, forcing the potassium hydroxide solution up into the pipette until it stands near the top of the broad portion where the bubbles break. There is left a thin layer of potassium hydroxide covering the bottom of the flask. The carbon dioxide which is not absorbed by this layer of potassium hydroxide passes up through the liquid in the pipette and is completely absorbed. After adding the hydrochloric acid the liquid in the distilling flask is heated and finally boiled for five minutes, the steam condensing and falling into the flask B. As can be seen by the construction of the apparatus, there is no backing up of the potassium hydroxide solution into the condenser even when the flame is entirely removed. This boiling drives the residual carbon dioxide into the absorbing flask where it is completely absorbed. If there is any doubt



as to the last portion of carbon dioxide in the flask B having been absorbed, the flask is shaken for a minute or two after disconnecting it and while holding a finger over the opening of the glass tube.

After distilling steam over for five minutes the writer

has always found the carbon dioxide to have been completely absorbed.

The stopper with the pipette is now partly withdrawn from the flask B, the pipette rinsed out several times into the flask and water added to the 100 cc. mark. After mixing, a 25 cc. portion is taken for titration. The advantages of this apparatus are as follows:

1. Ease of construction.

2. Ease of manipulation.

3. It permits of distilling over as much of the liquid as desired, to drive out the residue of carbon dioxide, without experiencing any annoyance due to sucking back of the potassium hydroxide solution into the condenser.

4. It eliminates the necessity of transferring the alkaline solution to another vessel before making it up to a definite volume, thus also keeping it away from contact with the carbon dioxide of the air.

The following table shows some results obtained with the apparatus here described.

SAMPLE.	CO_2 FOUND.	PER CENT.
Na_2CO_3	By direct titration	39.40
Na_2CO_3	By distillation and titration:	
Na_2CO_3	1st run	39.40
Na_2CO_3	2nd run	39.45
Baking powder No. 1	Available CO_2, 1st distillation	8.10
Baking powder No. 1	Available CO_2, 2nd distillation	8.02
Baking powder No. 1	Available CO_2, 3rd distillation	8.10
Baking powder No. 1	Total CO_2, 1st distillation	11.01
Baking powder No. 1	Total CO_2, 2nd distillation	10.91
Baking powder No. 2	Available CO_2, 1st distillation	8.76
Baking powder No. 2	Available CO_2, 2nd distillation	8.62
Baking powder No. 3	Available CO_2, 1st distillation	10.74
Baking powder No. 3	Available CO_2, 2nd distillation	10.91
Limestone	Gravimetric method	40.25
Limestone	Volumetric, 1st titration	40.23
Limestone	Volumetric, 2nd titration	40.40

When the method is used for the determination of the available carbon dioxide in baking powders, where it is necessary to decompose the sample with water, frothing occurs during the heating of the solution. This makes it difficult to distil over enough water to drive out the last of the carbon dioxide. In order to overcome this difficulty, when the distillation was carried as far as was practicable, the distilling flask was filled with water through the dropping funnel, thus forcing any carbon dioxide into the absorbing flask.

By using a solution of 25-30 per cent. alcohol instead of pure water, for decomposing the baking powder, it was found possible to prevent excessive frothing.[1] One could then clear the flask of the last portion of carbon dioxide by distilling over a little of the liquid and thus do away with the necessity of filling the flask with water.

It is necessary to determine the carbon dioxide in the potassium hydroxide solution used as the absorbing reagent and to apply the correction in each titration.

In the writer's experience with the volumetric method for carbon dioxide the greatest source of error is in the titration. The end point with phenolphthalein must be approached with care as the disappearance of the red color is rather slow.

ITHACA, NEW YORK.

[1] For this improvement of the method, the writer is indebted to Prof. G. W. Cavanaugh of Cornell University.

A MODIFICATION OF THE SWEENEY METHOD FOR CRUDE FIBER.

By CORNELIA KENNEDY.

Received May 6, 1912.

The method for the determination of crude fiber as recently modified by M. O. Sweeney[1] does not prove entirely satisfactory for all kinds of feed stuffs, especially those which are rich in protein. In his method an ether extracted sample of feed is first boiled for 30 minutes with 1.25 per cent. sulphuric acid. This acid solution is neutralized with 10 per cent. sodium hydroxide and 200 cc. of a boiling 2.65 per cent. sodium hydroxide solution added and boiled for 30 minutes. The sample is then filtered, washed, dried, weighed, incinerated and reweighed.

The acid dissolves certain nitrogenous bodies, pentosans, gums, etc., and when the alkali solution is added a heavy precipitation of some of these materials is caused. This precipitate is weighed with the crude fiber and consequently materially increases the percentage amount of fiber.

The following modification of the Sweeney method does away with this difficulty and gives results which check, within the limits of error, with the official method.

As in the above method the prepared sample is first boiled with 200 cc. of a 1.25 per cent. sulphuric acid. Neutralization is done away with, by making the alkali solution of such strength that it both neutralizes the acid and leaves the 400 cc. of 1.25 per cent. sodium hydroxide; 200 cc. of a boiling 3.52 per cent. sodium hydroxide are therefore added, and the whole boiled 30 minutes. The solution and fiber are then thrown onto a linen filter (which works more rapidly than a gooch because of the nature of the solution) and washed free of alkali. (Suction may be used to

	Official method.		Sweeney's method.			Sweeney's modified.		
	Per cent.	Average.	Per cent.	Average.	Increase over official method.	Per cent.	Average.	Increase over official method.
Bran	12.04		14.21			12.47		
	11.49	11.76	14.06	14.13	2.37	12.20	12.33	0.57
	0.55		0.15			0.27		
Sucreen food	14.33		15.92			14.67		
	13.92	14.12	15.58	15.75	1.63	14.43	14.55	0.43
	0.41		0.34			0.24		
Sugar and flax feed	6.90		7.44			7.12		
	6.89	6.90	7.44	7.44	0.54	7.08	7.10	0.20
	0.01		0.00			0.04		
Oil meal	7.87		10.20			8.81		
	7.86	7.87	10.08	10.14	2.27	8.80	8.81	0.03
	0.01		0.12			0.01		
Bran	11.37		12.95			11.81		
	11.11	11.24	12.94	12.95	1.71	11.69	11.75	0.51
	0.26		0.01			0.12		

[1] U. S. Dept. Agr., Bur. of Chem., *Bull.* **137**, 157.

cause a more rapid filtration.) The fiber is then thoroughly washed with boiling 1.25 per cent. sulphuric acid, which will remove the material precipitated by the addition of the alkali, washed free of acid, removed from the linen filter to a crucible, dried, weighed, incinerated and reweighed.

The Sweeney method has a great advantage over the official method by doing away with a filtration and thus saving time. This advantage is preserved in the modification of the Sweeney method.

The preceding table shows the results of all three methods on 5 different samples of feeds.

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STUDIES ON SOIL HUMUS.

By Sherman Leavitt.

Received January 30, 1912.

Humus is recognized as one of the most valuable constituents of a soil and yet little is known as to its composition. Fifty or sixty years ago, chemists thought they had shown humus to have a definite chemical composition with percentages of carbon, hydrogen, nitrogen and oxygen constant. According to their theory, humus was a salt of humic acid (also considered a definite chemical compound) which, upon oxidation, yielded simpler hypothetical organic acids called crenic and apocrenic. Although, as far as the writer knows, they had little or no experimental proof, many of these theories have been held to by some until quite recently.

In spite of all the work which has been done during the past fifty years, but little is known about humus. It is the belief of the writer that most chemists who have worked on the subject within the last fifteen years will agree that it is far from being a definite compound, and, in fact, that it is as variable in composition, if indeed not more so, as the different soils of which it is a component part.

Why does soil *A* accumulate humus matter readily while soil *B*, under similar conditions of treatment, etc., apparently makes no appreciable and permanent improvement?

We are working at this problem along two general lines: First, under field conditions; second, under laboratory control.

This article will be confined mainly to the second class, as definite results from the field cannot be obtained under many years.

In the laboratory, large samples of soils that are under field experimentation are being used. These were procured from car-load lots, thoroughly mixed, so that the samples are quite representative of the types under investigation. These samples represent four distinct type soils in different sections of Tennessee and were chosen for the reason that each one was the poorest soil of that particular type. It was thought of interest to include a Florida Everglade soil, rich in humus, for comparison in the chemical work.

As most of the humus matter in Tennessee soils is present in the first six inches of soil, the laboratory work on humus has been confined to this layer.

At the beginning of this work it was deemed advisable to remove completely, under the same conditions of extraction, the humus matter from a large quantity of each one of these soils. Under similar conditions of preparation, the humus matter obtained from each one of these soils ought to be at least approximately comparable. Any appreciable difference in the approximate composition of the several samples of humus might have great significance and might point to some quite different behavior of the humification process in the several soils. This may be taken as the key-note of the following investigation:

A number of quantitative chemical methods for the determination of percentage of humus in soils were subjected to examination for their respective values. The investigation earlier reported[1] brought out some valuable points, notably that the humus matter from different soils could be absolutely different both in appearance and in behavior toward reagents. Several of the methods in use for the determination were found unreliable on Tennessee soils for the reason that they failed to show all of the organic matter in the ammonia solutions.

In this later investigation, dealing more specifically with the properties of the several humus samples, a description of the method of procedure in the preparation of the samples of humus will be given. During the work, it was deemed advisable to modify the method of removing clay from the samples, the reasons for which will be given.

Method A.—Five hundred grams of the air-dried soil were extracted with 1 per cent. hydrochloric acid, according to the Official Method, washed free from acid and then extracted three days with 4 per cent. ammonia, allowed to settle and the supernatant liquid drawn off. Fresh 4 per cent. ammonia was added and the process repeated. The soil was extracted three times with successive portions of 4 per cent. ammonia, about two liters of solution being used for each extraction. The last extraction contained very little coloring matter. The extractions were all evaporated to dryness in a large porcelain dish on the hot water bath, baked for some hours, and cooled. The residue was then extracted with about two liters of 4 per cent. ammonia, washed by decantation and filtered. A large proportion of the flocculated clay was retained on the filter paper, which was thoroughly washed with 4 per cent. ammonia. The process of evaporation, baking, extraction, washing and filtering, was repeated a number of times until the filtrate appeared absolutely clear. This was then evaporated to dryness in a large beaker to drive off the excess of ammonia; dissolved in hot, distilled water; filtered and washed into a 500 cc. graduated flask; cooled and 1 cc. of strong ammonia added to prevent fermentation; then made up to the mark. The solution was thoroughly mixed and allowed to stand for two months to give finely divided clay, still in suspension, a chance

[1] "Soil Humus as Determined by Different Methods," This Journal, **2**, 269.

to settle out. The supernatant solution was pipetted off for analysis and the amount of humus and ash present determined in 10 cc. portions.

All of the preliminary work was carried on with the humus prepared as above until the supply was exhausted. Fearing a possible hydrolysis of some of the organic compounds might have taken place during the many evaporations to dryness and baking of the humus matter, it seemed wise in making up new samples of humus to modify the method of removing clay so as to reduce the chance of hydrolysis to as low a figure as possible.

Since this change was decided upon, the Illinois Experiment Station has published Stewart's doctoral thesis as *Bulletin* 145 of that Station. Among the general conclusions reached, the author says: "The evaporation on the water bath of the ammoniacal solution, in the preparation of the *matiere noire* in quantity for analysis, causes a hydrolysis of the organic phosphorus compounds." This would seem to confirm the fear of possible hydrolysis of some of the organic compounds other than organic phosphorus compounds.

The modified method of removing clay decided upon depends almost entirely on long settling of the solution for the removal of most of the clay, instead of baking on the steam bath, as in Method A. It was also deemed advisable to make all concentrations and evaporations at not over 60° C., final concentrations to be made in a partial vacuum, taking care never to allow the solution to become more concentrated than 700 cc. During the greater part of the evaporation, the volume of the solution was kept at approximately two liters and was not brought below one liter until the final concentration, the excess of ammonia by that time being expelled. Fortunately, this slow evaporation with constant additions of cold fresh solution to the evaporating solution tends to flocculate the clay left in suspension.

Method B.—Twenty-two hundred and seventy grams (approximately 5 pounds) of soil were extracted as under Method A, proportionately larger amounts of acid and 4 per cent. ammonia being used. Reverse filtration through fine mesh linen and the siphon were used as much as possible to avoid handling the great bulk of clay. This solution was transferred to large, deep, tightly-stoppered jars and allowed to stand undisturbed for about three months, until the supernatant liquid was quite clear. The solution was then siphoned off and filtered, first through coarse filter paper and then through S & S special hardened and toughened filter paper No. 575, suction being used toward the end of the operation. The paper, with removed clay, was thoroughly washed with 4 per cent. ammonia to make sure that all organic matter was obtained. The residual clay gave no indication of occluded organic matter on being baked on the bath and extracted with ammonia according to Mooers and Hampton's method.[1] The evaporation and concentration of the filtrate and washings were carried on between 50° and 60° C., as described in the above paragraph. When the filtrate and washings were concentrated to about 700 cc., they were filtered into a liter graduated flask and the paper thoroughly washed with warm water. The whole solution was now cooled and made up to the mark and 1 cc. of chloroform added as a preservative. The flask was placed aside to stand several months before use, to allow additional finely divided clay an opportunity to deposit. The filtrations at best were mostly slow and troublesome, especially the earlier ones. In order to obtain humus satisfactorily by this method, at least six months were required for the proper preparation of samples.

An investigation of this kind is, for many reasons, extremely difficult. As we have already seen, the preparation of samples for comparison is a tedious process, requiring abundant time and patience. The resulting samples are complex in structure and practically nothing is known of them.

As a preliminary investigation of the subject, a study was made of the effect of different mineral elements, such as calcium and iron, on humus in water solution. Some of the richest soils in Tennessee are of the red type, high in iron and very retentive of humus matter.

For this reason it seemed advisable to study the effect of iron in its different states of oxidation, as *ic* and *ous* iron on the removal of humus matter from water solution. Humus prepared from both good and poor soils was used. Some interesting results were obtained which, however, will need further confirmation. As a matter of interest, these results have been inserted and will be discussed briefly. The writer, however, does not wish to lay stress on the results or the conclusions drawn until they are borne out by more extensive work.

TABLE I.

Character of soil.	Laboratory number.	Humus in soil.	Humus by ferric iron.	Humus by ferrous iron.	Humus by calcium chloride.
		Per cent.	Per cent.	Per cent.	Per cent.
Good.....	916	1.46	60.39	65.06	41.10
Good.....	819	1.29	66.67	64.34	45.74
Good.....	1206	5.11	61.65	73.19	42.67
Good.....	1267	1.66	65.82	57.14	49.74
Poor.....	1266	0.39	69.63	83.22	53.57
Poor.....	844	0.52	48.07	39.65	42.31
Poor.....	867	0.87	22.96	44.82	18.40
Poor.....	1096	0.93	46.61	85.92	64.22
Poor.....	1101	0.90	28.15	66.81	40.76

In connection with the above work, it is interesting to note that the analysis of the humus ash of a Florida soil, which had 9.56% of humus, showed an ash content of 21.4 per cent. ferric oxide.

Ferrous iron precipitated more humus matter than ferric iron from the same humus samples, in two-thirds of the soils experimented with. Out of nine soils, four of which were classified as good, having from 1.30 per cent. to over 5.00 per cent. of humus, and five soils ranked as poor, having less than 1.00 per cent. of humus, with one exception ferric iron precipitated 20 per cent. more from the humus of the good soils than from the humus of the poor soils.

Calcium, in the form of chloride, was found to pre-

[1] *J. Am. Chem. Soc.*, **30**, No. 5 (1908).

cipitate less humus matter from good soils than either form of iron.

In all of the above cases, organic matter was left in solution. This could be removed as a copper salt more or less completely, when the solution was slightly acid and after the removal of any interfering element, such as excess of iron. This result is quite similar to the writer's finding in the first paper on the subject,[1] where it was noted that a precipitate of organic matter with copper was always obtained after a precipitation of humus matter with hydrochloric acid. It would seem possible that hydrochloric acid and ferric iron precipitate approximately the same substances.

sans. This result is very similar to the one obtained in this laboratory.

Pentosans were obtained, by the Official Method, from all samples of humus examined in this laboratory. This result is also fully in accord with the findings of Schreiner and Shorey,[2] who obtained pentosans in all ten soils examined by them. Our results varied from 1.74 per cent. in the case of the Florida soil (all percentages on the basis of humus and not on original soil) to 3.72 per cent. on the Gallatin soil; in terms of pentoses, the figures would be 1.99 per cent. to 4.22 per cent., respectively.

In the preparation of the samples of humus under method B, the 1 per cent. hydrochloric acid extracts

TABLE II.

Most of the results given are averages of from three to five determinations.

Location of soil.	Percentages on original soil. Humus in original soil.	Nitrogen in original soil.	Nitrogen in 1% hydrochloric acid extract.	Total nitrogen dissolved by 1% acid.	Weight of humus used for determination, ash not included.	Weight of ash not counted as humus.	Percentages on basis of humus. Proteids or like proteids ppd. by $(NH_4)_2SO_4$.	Starch-like bodies calculated to starch.	Furfural determination calculated to Per cent. pentoses.	Furfural determination calculated to Per cent. pentosans.
Cookeville, Tenn.	0.93	0.0730	0.0020	2.74	0.369	0.065	70.4	10.40	3.83	3.37
Crossville, Tenn.	0.90	0.0737	0.0014	1.90	0.238	0.013	33.6	8.37	4.14	3.64
Jackson, Tenn.	0.39	0.0560	Nitrogen present; partly lost.	Over 2.00	0.112	0.012	75.0	10.80	Present[2]	Present[2]
Gallatin, Tenn.	1.66	0.1350	0.0042	3.11	0.392	0.016	57.9	10.60	4.22	3.72
Florida Everglades, Fla.	9.56	1.750	0.0345	1.97	2.392	0.067	61.4	4.47	1.99	1.74

In all the samples examined, strong evidence was found of a carbohydrate body in amounts varying from 4.5 per cent. to 10.8 per cent., calculated as starch. This body is very similar to starch, although it gives no reaction with iodine.

Dilute, boiling, hydrochloric acid, according to the Sachsee method, hydrolyzed it to reducing sugars which were determined by Allihn's method, and for convenience calculated to starch. On treating the humus with diastase, with subsequent acid hydrolysis, we obtained practically the same results as by the direct acid hydrolysis. The original solutions of humus gave no reactions with Allihn's solution either before or after inversion with cold hydrochloric acid.

From the acid hydrolysis solution on a sample of humus obtained from a Florida Everglades soil, a crystallizable sugar was obtained which reduced Allihn's solution. Some of the mother liquor had no optical rotation and was easily fermentable. The solution, after fermentation, gave reactions for ethyl alcohol and acetic acid, and also continued to reduce Allihn's solution.

This crystallizable sugar, on account of its ease of fermentation, we classify as a hexose sugar, although it has not as yet been completely identified. Schreiner and Shorey[3] have recently obtained a pentose sugar by hydrolysis of a gummy mass precipitated by alcohol from a caustic soda extract of a soil high in pento-

[1] "Soil Humus as Determined by Different Methods," THIS JOURNAL, **2**, 269.

[2] Had enough solution for only a qualitative analysis.

[3] *Experiment Station Record*, **23**, No. 1, 11.

of the original soils were saved as completely as could conveniently be done. These were evaporated to dryness and, with some difficulty, determinations of nitrogen were made upon the total large residues. The determination on the Jackson soil was partly lost. It is interesting to note that in every case an appreciable amount of nitrogen was obtained in the 1 per cent. hydrochloric acid extract of the original soil. This, the writer believes, is contrary to the generally accepted opinion that there is no nitrogen in the 1 per cent. acid extract. This nitrogen is probably due to amino acids,[2] which are somewhat soluble in dilute mineral acids.

We must keep in mind the fact that these nitrogen determinations, as given in Table II, are all too low as a result of the inevitable loss in handling the large bulks of soil and extract. In the Tennessee soils under examination, a variation of from 1.9 per cent. to 3.1 per cent. of the total nitrogen in the soil was found to be soluble in 1 per cent. hydrochloric acid. This quite appreciable portion of the whole nitrogen is probably present as amino acids. It is not included as humus nitrogen.

In this paper the writer has tried to emphasize the following facts:

INVESTIGATION.

a. Two methods were used for the removal of clay in the preparation of large amounts of humus:

[1] *Experiment Station Record*, **23**, No. 1, 11.

[2] The writer is indebted to Professor W. R. Orndorff for this suggestion.

1. Moores and Hampton's method.

2. Mechanical separation, without evaporation, to dryness.

b. Preliminary indications were obtained of the relative behavior of ferric iron, ferrous iron and calcium in the retention of humus from water solution.

c. Protein or like-proteins were present in humus examined.

d. A starch-like body was present which can be hydrolyzed by acids and also acted upon by diastase with subsequent acid hydrolysis. Both of these processes gave reducing sugars, in comparable amounts, in all samples of humus examined.

e. One of these reducing sugars was obtained in a crystalline form but has not, as yet, been fully identified. This was obtained from the humus of a Florida soil.

f. Pentosans were present in appreciable amounts in all samples of humus examined.

g. Nitrogen, probably present as amino acids, was found in the 1 per cent. hydrochloric acid extract in all soils examined by the Official Method for the determination of humus.

The work was done at the Agricultural Experiment Station of the University of Tennessee, Knoxville, during the years 1909 and 1910.

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AN EXAMINATION OF CITY STREET SWEEPINGS.[1]

By J. J. SKINNER AND J. H. BEATTIE.

Received April 19, 1912.

The value of street sweepings is a matter that is of interest to officials of all the large cities. The débris which is collected from the streets of cities is commonly used as fertilizing material, being sold to near-by gardeners, truckers, and farmers, its rather low cost making it particularly attractive. The main object of the city official is to dispose of the material; in some cases it is burned and in others it is hauled to a dumping ground and used as filling material.

There is some variation in the character of the material collected from the streets of different cities, depending on the nature of the industries, the kind of paving material used, and the character of traffic on its streets, yet on the whole the collections from sweepings are very similar and consist chiefly of manure from animals, leaves, dirt, and trash, such as paper, fruit skins, particles of coal, etc. It is possible that the sweepings contain finer particles of the paving substance and some oily material dropped from vehicles. This is especially true at the present time, when the use of power vehicles for pleasure and business is so extensive. The effect of the sweepings on crops, especially when used continually year after year on the same fields, is one of much interest and has caused considerable speculation.

This article deals with an investigation of the street sweepings of one of the larger cities. The material has been studied from the point of view of its organic and inorganic constituents and through cultural tests, where its effects on plant growth was observed.

[1] From the Laboratory of Soil Fertility Investigations by permission of the Secretary of Agriculture.

CHEMICAL EXAMINATION FOR MINERAL SALTS.

Three samples of the sweepings were examined: sample No. 1 consisted of the débris secured by hand sweeping with a brush, sample No. 2 was that secured by sweeping with a machine, and sample No. 3 was the decomposed débris from a dump pile which had been accumulating for some length of time. There was no apparent physical difference between Samples No. 1 and No. 2, both being composed mostly of the raw horse manure. Sample No. 3 consisted principally of well-decomposed horse manure. The chemical analysis of the three samples is given in Table I, the results being stated in per cents. of dry material. The analyses were made by Mr. J. G. Smith, of the Laboratory of Physical and Chemical Investigations:

TABLE I.—ANALYSES OF STREET SWEEPINGS.

Number and description.	Nitrogen (N). Per cent.	Potash (K_2O). Per cent.	Phosphate (P_2O_5). Per cent.
1 Hand sweepings	1.34	0.71	1.03
2 Machine sweepings	0.86	0.55	0.55
3 Decomposed sweepings	0.60	0.56	0.60

This table shows each of the samples to contain appreciable amounts of nitrogen, potash, and phosphate, sample No. 1 being somewhat higher in each of these fertilizing constituents. Stable manure as determined from an average of a large number of samples[1] contains about 1.6 per cent. of nitrogen, 1.5 per cent. of potash, and about 1.00 per cent. of phosphoric acid, the figures being based on dry material. Comparing these amounts with that contained in ordinary horse manure from the stable, it will be seen that the content of nitrogen, potash and phosphate is higher in the latter. The lower result might be expected, as the sweepings are not all horse manure, but contain considerable foreign material, aside from the fact that they are frequently subjected to leaching by rain.

EFFECT ON GROWTH.

The efficiency of street sweepings and other manures of this nature as fertilizing material should not be judged merely by the percentage of mineral salts which they contain. The organic material itself has an important bearing on the question, as it may be of such a nature or contain constituents which cause it to have either a beneficial or harmful effect on soils.

Experiments were undertaken to test the effect of sweepings on crops, by growing plants in soil to which they had been added. In these experiments an especially constructed paraffine wire pot,[2] possessing certain advantages over the ordinary clay pot, was used.

To test the effect of sweepings on soil, wheat was grown in the paraffine wire pots for one month. The soil used in the test was a clay loam. The soil was divided into four portions. To three of these was added a sample of one of the three types of sweepings, while to the fourth good stable manure was added

[1] Storer, F. H., "Agriculture in Some of its Relation with Chemistry."

[2] For description of method, see *Circular* **18**, Bureau of Soils.

in order that a comparison might be made. These cultures were checked against the growth in untreated soils. The sweepings and manures were used at the rate of 5 tons per acre. The tests were conducted in a green-house, where the conditions of temperature and moisture could be controlled. When the plants had grown for 30 days, they were cut and the green weight recorded. Three pots were used for each treatment, six plants in each pot.

TABLE II.—GROWTH OF WHEAT IN SOIL TREATED WITH STREET SWEEPINGS AND STABLE MANURE.

Treatment.	Green weight. Grams.	Increase. Per cent.
Soil untreated	1.708	
Soil + hand sweepings (Sample No. 1)	2.240	31
Soil + machine sweepings (Sample No. 2)	1.880	10
Soil + decomposed sweepings (Sample No. 3)	1.800	5
Soil + stable manure	2.500	46

The figures in this table show the sweepings to be beneficial, especially sample No. 1, but not as efficient as good stable manure.

Another test was made in which corn was grown in the soil treated with street sweepings and stable manure, the manurial treatments and general methods being the same as in the first experiment. Results which substantiate those obtained in the latter were secured. The green weight is given in the table below:

TABLE III.—GROWTH OF CORN IN SOIL TREATED WITH STREET SWEEPINGS AND STABLE MANURE.

	Green weight. Grams.	Increase. Per cent.
Soil untreated	3.700	
Soil + hand sweepings (Sample No. 1)	4.710	27
Soil + machine sweepings (Sample No. 2)	4.160	12
Soil + decomposed sweepings (Sample No. 3)	3.440	—8
Soil + stable manure	4.950	34

There was an increased growth with samples No. 1 and No. 2, but a decrease where sample No. 3 was used. Again the stable manure had a more beneficial effect than the best of the sweepings. The growth is shown in Fig. 1.

Another culture test was made, using a vegetable

FIG. 1.—EFFECT OF STREET SWEEPINGS AND STABLE MANURE ON CORN.

(1) Soil untreated; (2) soil + stable manure; (3) soil + sweepings No. 1; (4) soil + sweepings No. 3; (5) soil + sweepings No. 2.

(radish) as the plant on which to test the effect of the street débris. The growth of plants in this experiment is shown in Fig. 2. Again the sweepings are beneficial, the plants in Pots Nos. 2, 3 and 4 being larger than in the untreated Pot No. 1. Pot No. 4, which contains the soil treated with decomposed sweepings, has smaller plants than any other except the check. It will be recalled that this treatment showed the least effect also in the case of wheat and corn. Pot No. 5, which is treated with

FIG. 2.—EFFECT OF STREET SWEEPINGS AND STABLE MANURE ON RADISHES.

(1) Soil untreated; (2) soil + sweepings No. 1; (3) soil + sweepings No. 2; (4) soil + sweepings No. 3; (5) soil + stable manure.

stable manure, has produced the largest growth, which again shows that the sweepings are not as helpful as good stable manure.

EXAMINATION FOR MINERAL OIL.

As was pointed out, the sweepings are apt to contain lubricating oils and fine particles from the decay of the paving materials, which may be a factor in determining their usefulness as a fertilizer material. In order to study this point the three samples were repeatedly extracted in an extraction apparatus with petroleum ether until the solvent was no longer colored. The fatty material was saponified with alcoholic potash and the amount of mineral oil extracted by petroleum ether determined. Sample No. 1 contained 1.7 per cent., sample No. 2 2 per cent., and sample No. 3 2 per cent. of the crude mineral oil. This high content of mineral oil suggests the possibility of the recovery of low-grade lubricating oil from city street sweepings, especially in those cities which have considerable automobile traffic.

EFFECT OF THE OIL ON GROWTH.

The effect of the oil extracted from the sweepings was tested with wheat plants. Young wheat seedlings were grown in distilled water and nutrient solution cultures. Fifty milligrams of oil from each sample were put in the culture bottle containing 250 cc. of solution. The oils from all of the samples were harmful to growth, the roots as well as the tops being affected. Oils from samples No. 1 and No. 2 reduced the growth of wheat 10 per cent. in the case of the distilled water cultures, and the oil from sample No. 3 reduced the growth 20 per cent. In the solution containing the nutrient salts, the oils used in the same amount, from sample No. 1 reduced growth 6 per cent., from sample No. 2 7 per cent., and from sample No. 3 11 per cent.

TEST OF SWEEPINGS AFTER OIL WAS EXTRACTED.

The sweepings from which the oils had been extracted were next tested as to their effect on growth. The petroleum ether was evaporated completely from the manure by allowing it to stand in the open for a week or more. The same kind of soil was used as in the previous experiments and the extracted sweep-

mgs were added to portions of the soil at the rate of 5 tons per acre. Treatments with stable manure, extracted with petroleum ether and also in its natural condition, were included in the test as a means of comparison with the samples of sweepings. The plants were grown in the paraffine pots for 30 days, then the green weights were taken. Three pots were used for each treatment. The growth is given in Table IV.:

TABLE IV.—EFFECT OF STREET SWEEPINGS, AFTER BEING EXTRACTED WITH PETROLEUM ETHER.

Treatment.	Green weight of Wheat. Grams.	Radish. Grams.
Soil untreated	1.910	3.700
Soil + hand sweepings, extracted (Sample No. 1)	2.270	5.400
Soil + machine sweepings, extracted (Sample No. 2)	2.270	5.700
Soil + decomposed sweepings, extracted (Sample No. 3)	2.190	5.200
Soil + stable manure, extracted	2.260	5.800
Soil + stable manure, natural	2.270	5.700

An examination of the figures in the table shows that the sweepings and stable manure had about the same efficiency in causing increased growth; this is true with both the grain and the vegetable crop. The oil was also extracted from the sweepings by using ether as the solvent and the sweepings afterwards tested in soils. This test also showed that the sweepings were practically as good as the stable manure.

It will be recalled that the effect of the unextracted sweepings was not nearly so good as the effect produced by the stable manure. In other words, after the oil was removed from the street débris its action was practically the same as that of the stable manure. That the oil is the deleterious constituent of the sweepings is also borne out by the fact that the oil itself, when added to culture solutions in which plants were growing, markedly reduced their growth.

The application of street sweepings to soils will undoubtedly have a beneficial effect and be a factor in building up the land; the possible danger of a harmful effect from the oily substance which it contains must, however, be considered. If the oil could be economically extracted this danger would be averted. The oil in the débris for the first year or two may not have any effect, but a continuous application to a field year after year may eventually impair its productiveness, unless through drainage or other natural agencies the oily material is drained off or changed. In some localities this is probably the case, as the use of such material is still said to be effective, although it has been applied for a number of years. No very definite field information on this point is, however, at hand. In this connection attention must be called to the fact that the presence of an unusual amount of oil in such street sweepings has been the result of automobile traffic, and hence appears only in recent years as an appreciable factor in the use of street sweepings as fertilizer, and it is not improbable that the amount of oil will even further increase in the next few years.

Aside from the physiological action of the oily material here mentioned, there are probably other more strictly physical effects due to the coating of soil particles, thus interfering with normal moisture movements and solubility of the mineral soil constituents.

Vegetable or animal oils undergo changes in soils under the influence of soil organisms, but so little is known concerning the action of organisms on the strictly hydrocarbon oils that no statement concerning the possible disappearance or change of this oil in street sweepings can be made.

BUREAU OF SOILS,
WASHINGTON, D. C.

INORGANIC PHOSPHORUS IN PLANT SUBSTANCES—A METHOD OF ESTIMATION.

By R. C. COLLISON.

Received May 15, 1912

In the synthesis of organic phosphorus compounds by the plant and their storage in seeds as reserve food, the inorganic phosphates play an important part. The phosphorus used in this synthetic process is taken into the plant in inorganic form and used in the building up of complex organic phosphorus compounds such as lecithins, phospho- and nucleo-proteids and salts of phytic acid.

It is believed by some investigators that unmodified plant tissue and a large number of the seeds contain practically no phosphorus in inorganic combination. Since inorganic phosphate is the starting point in the synthesis of organic phosphorus compounds and as there exist in the plant enzymes which have the property of splitting off inorganic phosphorus from such compounds, it would seem probable that at least an appreciable quantity of phosphorus in inorganic form might be found in such plant tissues and seeds.

It is doubtful whether the failure to demonstrate the presence of appreciable quantities of inorganic phosphorus in seeds has been due to its absence in the plant substance under examination or to analytical methods, which may be questioned from a chemical and practical standpoint.

Methods of estimating inorganic phosphorus in plant substances usually begin with some means of acid extraction of the material, with subsequent separation of the phosphates from the extract. Some of the proposed methods may be questioned on the ground of mechanical imperfection and also because they do not take into sufficient consideration the influence of organic matter on the precipitation of phosphates with the common precipitating agents. This influence on precipitation was investigated, to some extent, by the author two years ago.[1]

Dilute acid extracts of plant substances contain, besides inorganic salts, also proteids, carbohydrates and, in the case of cereals, salts of phytic acid. The proteids and carbohydrates both inhibit the formation of ammonium-phosphomolybdate, and the salts of phytic acid especially have the property of suppressing the formation of this precipitate in a marked degree. The influence of phytin, especially, was investigated by the author two years ago. That it is no

[1] *Bull.* **215**, Ohio Agr. Exp. Sta., April, 1910.

small factor contributing to the accuracy of the final results can be readily appreciated when the results below, which were secured at that time, are examined.

Commercial phytin was dissolved in 0.2 per cent. nitric acid and pure sodium phosphate, equivalent to 0.0420 gram magnesium pyrophosphate, added. Acid molybdate solution in excess was then added and the solutions digested at 60° C. for one hour. The volume of the solutions was about 200 cc.

TABLE I.[1]—INFLUENCE OF PHYTIN ON THE PRECIPITATION OF PHOSPHORUS.

Grams phytin.	Grams pyrophosphate recovered.
1.0	0.0000
0.5	0.0260
0.4	0.0329
0.3	0.0371
0.0	0.0420

Phytin is only one of the substances present in acid extracts of seeds, which may have a retarding or inhibiting influence on the precipitation of phosphorus. Large quantities of some salts of organic acids seem to have this tendency. Alkaline citrates, solutions of which seem to have the property of dissolving phytin, have tendencies in this direction.

These results, it is believed, indicate very clearly that failure to demonstrate the presence of inorganic phosphorus in some of the seeds may easily have been due to discrepancies in the analytical methods.

There is no absolute standard with which we can compare results by different methods. The only standard we have for comparison is one established by the addition of a known quantity of pure phosphate to a plant substance, together with the constancy of our analytical results. Complete recovery of the phosphorus added and a constant result for inorganic phosphorus without such addition constitutes the most reliable test we have at present of any given method.

The difficulties in precipitation above noted have been, to some extent, overcome by some previous work two years ago.[1] A brief description of the method published at that time is here given.

Ten grams of the substance are extracted with 300 cc. of 0.2 per cent. hydrochloric acid for three hours: 250 cc. of the filtered extract are precipitated with magnesia mixture and made strongly ammoniacal. After 12 hours the precipitate is filtered off and washed with ammonia and finally with alcohol. The dried paper with the precipitate is thoroughly shaken with a measured volume of acid alcohol, the mixture filtered, an aliquot of the filtrate evaporated and phosphorus determined in the residue.

This method avoids the necessity of precipitating phosphorus in the presence of proteids and salts of phytic acid. It has now been in use for two years in this laboratory and has given more satisfactory results than any method previously used.

In all the plant substances examined from time to time, appreciable quantities of inorganic phosphorus have been found by this method. A few results are here given for illustration:

[1] *Bull.* **215**, Ohio Agr. Exp. Sta.

TABLE II.—TOTAL AND INORGANIC PHOSPHORUS IN A FEW PLANT SUBSTANCES.

Substance.	Total phosphorus. Per cent.	Inorganic phosphorus. Per cent.
Oats, grain	0.397	0.060
Wheat, grain	0.394	0.036
Corn, grain	0.266	0.041
Soya beans	0.547	0.054
Cow peas	0.445	0.056
Rice polish	0.600	0.027
Alfalfa hay	0.230	0.136
Blue grass	0.256	0.158

With substances giving extracts low in organic material, as is the case with the rough feeds, such as the hays, and also with many other substances, the method gives very consistent results. With substances giving extracts high in organic material, this method may cause high results due to great difficulty in filtering the extracts, the prolonged standing probably causing decomposition of organic phosphorus compounds, and in other cases low results due to the influence of organic substances on precipitation of magnesium-ammonium-phosphate.

These difficulties are met with especially in the extracts of leguminous seeds, cereal grains and their by-products, which are in general very difficult to filter.

With the purpose of eliminating these sources of objection a new method is proposed, which, although bearing some resemblance to the old method in its minor details, is quite different as regards extractive medium and method of precipitation.

While investigating the solubilities of inorganic and organic phosphorus compounds in connection with the acid water extraction method, the author found that cold acid alcohol (94 per cent. alcohol containing 0.2 per cent. of hydrochloric or nitric acid) has the property of dissolving the common phosphates, which are insoluble in neutral or slightly alkaline alcohol. Proteids in general, nucleinic acid from yeast, carbohydrates and salts of phytic acid appear for the most part to be insoluble. Taking these facts into consideration, an acid alcohol extraction of the material is proposed. Such an extraction would insure solution of inorganic phosphates, which could be filtered from the undissolved organic phosphorus compounds in the residue.

For the investigation of this proposed method of extraction and separation three plant substances were selected.

(1) Soya beans, on account of their high percentage of soluble protein and also because dilute acid water extracts of the ground beans, as well as the precipitated extracts, are extremely difficult to filter.

(2) Rice polish, on account of its rather high content of phytin.

(3) Corn germ meal, on account of its content of nuclein phosphorus.

The method of procedure and the new method in detail, as proposed, is as follows:

NEW METHOD OF ACID ALCOHOL EXTRACTION IN DETAIL.

A ten-gram sample of the substance, very finely ground, is placed in a 400 cc. Florence flask and covered with exactly 300 cc. of 94 to 96 per cent. phos-

phorus free alcohol, which contains 0.2 per cent. of hydrochloric acid (calculated from the per cent. HCl in the concentrated acid). The flask is shaken at intervals of five minutes for three hours. The extract so obtained is then filtered through dry double 11 cm. filters into dry flasks. No suction is necessary. An aliquot of 250 cc. of this filtrate is placed in a 400 cc. beaker and made just alkaline to litmus paper with ammonia. A slight excess of ammonia does no harm. The solutions are allowed to stand 8 to 12 hours or overnight and then filtered through double 11 cm. filters, care being taken to decant the clear liquid as long as possible. The precipitate is then transferred to the filter and washed with 94 to 96 per cent. alcohol, which has been made very slightly ammoniacal. In transferring the precipitate, some of the material may stick very tenaciously to the beaker. In this case, after cleaning the beaker fairly well, add 5 drops of hydrochloric acid to the beaker, rub out the latter with a rubber tipped rod, add 10 cc. of alcohol and then make just alkaline with ammonia and transfer this last portion to the filter. In this way the last traces of the precipitate can be easily removed. After washing several times, the inner filter with the precipitate is spread out and allowed to dry completely. It is then transferred to an Erlenmeyer flask containing exactly 100 cc. of 0.5 per cent. nitric acid in water (calculated from the per cent. HNO_3 in the concentrated acid). The flask is stoppered and the contents thoroughly shaken until the paper and precipitate are broken up. It is best to let stand for some hours. The material in the flask is then filtered through dry double 11 cm. filters into dry beakers and exactly 75 cc. of the filtrate precipitated with 50 cc. of official acid molybdate solution in the usual way. Ten grams ammonium nitrate and two hours digestion at 60° C. are usually sufficient. The final result represents the amount of inorganic phosphorus in 6.25 grams of the original sample.

It is advisable to reprecipitate the pyrophosphate, if the final solutions are highly colored, which is sometimes the case with some of the rough feeds, as the hays. In the case of substances which are relatively high in inorganic phosphorus, a smaller sample may be taken, 3 to 6 grams. In using this method with substances which are tenacious and gummy, and which do not break up readily in acid alcohol, as is true of dried fruits and other substances containing considerable sugar, the same may be worked up with sand and a definite quantity of water, 15 to 20 cc., is usually sufficient. This may be done in a mortar and the material washed out into the flask with acid alcohol, care being taken to use the correct volume, namely, 300 cc. minus the quantity of water used. This method deflocculates the most refractive substances in this regard. It is also very important to have the original material ground as fine as possible before extraction.

Three sets of determinations were made by this method on soya beans, rice polish and corn germ. In each case determinations were made with and without the addition of a known amount of pure phosphate, in an endeavor to recover the latter completely.

The first two sets of results were slightly low, due to insufficient time given for precipitation, since the filtered extracts were made ammoniacal and filtered immediately. Following the detailed method as stated, allowing the extracts after precipitation to stand the specified 12 hours, very consistent results were obtained as shown by the following table:

TABLE III.—RECOVERY OF ADDED PHOSPHORUS BY ACID-ALCOHOL EXTRACTION METHOD.

Substance	Without phosphate.	With phosphate 0.0037 gram phosphorus.	Theoretical results.	Per cent. inorganic phosphorus.
Soya beans	0.0015	0.0053	0.0052	0.024
Rice polish	0.0012	0.0048	0.0048	0.019
Corn germ	0.0018	0.0053	0.0054	0.028

The figures are grams of phosphorus (element) and are averages of three determinations.

The first column of figures represents the quantity of inorganic phosphorus found in the material itself. Column 2 represents the amount found after the addition of pure phosphate in known quantity, and column 3 the results which should have been obtained after adding pure phosphate, assuming that the figures in column 1 are the correct ones for inorganic phosphorus. For example, the inorganic phosphorus in 6.25 grams of soya beans amounted to 0.0015 gram phosphorus. To every 6.25 grams of sample were added pure sodium phosphate equivalent to 0.0037 gram phosphorus. Thus, if the added phosphorus were completely recovered, the result should have been 0.0015 + 0.0037 = 0.0052 gram phosphorus for the theoretical.

These results check with the theoretical as closely as could be desired, indicating complete recovery of the phosphate.

In Table IV are given similar results on a more extended scale. The pyrophosphate was reprecipitated, the results being given in column 3.

TABLE IV.—INORGANIC PHOSPHORUS BY NEW METHOD, WITH AND WITHOUT PURE PHOSPHATE.

Substance.	Without phosphate.	With 0.0037 gram phosphorus.	With phosphate reprecipitated.	Theoretical results.	Per cent. inorganic phosphorus.
Cow peas	0.0014	0.0053	0.0051	0.0051	0.023
Oil meal	0.0017	0.0057	0.0053	0.0054	0.027
Corn meal	0.0016	0.0056	0.0051	0.0053	0.025
Wheat, grain	0.0008	0.0046	0.0044	0.0045	0.012
Wheat bran	0.0021	0.0063	0.0060	0.0058	0.034
Wheat germ	0.0025	0.0068	0.0064	0.0062	0.040
Clover hay	0.0043	0.0085	0.0082	0.0080	0.070
Timothy hay	0.0030	0.0068	0.0067	0.0067	0.047
Oats, grain	0.0026	0.0067	0.0064	0.0063	0.041
Cottonseed meal	0.0014	0.0055	0.0053	0.0051	0.023
Rice polish	0.0012	0.0050	0.0049	0.0049	0.019
Corn germ	0.0018	0.0055	0.0055	0.0055	0.029
Soya beans	0.0015	0.0053	0.0052	0.0052	0.024

The figures represent grams of phosphorus (element).

Here again the results agree with the theoretical in every case.

The extracts of substances which by the acid water extraction method filter with great difficulty, by the acid alcohol extraction method filter with great ease, as well as the solutions after precipitating by neutralization.

In order to make the comparison complete, a similar series of determinations was made by the acid water extraction method on the same substances, with and without phosphate added.

TABLE V.—COMPARISON OF ACID WATER AND ACID ALCOHOL EXTRACTION METHODS. RESULTS BY ACID WATER METHOD

Substance.	Without phosphate.	With phosphate, 0.0081 gram phosphorus.	Theoretical results.	Per cent inorganic phosphate, acid water extn.	Per cent. inorganic phosphorus, acid alcohol extraction.
Cow peas	0.0013	0.0068	0.0094	0.020	0.023
Oil meal		Unfilterable			0.027
Corn meal	0.0014	0.0092	0.0095	0.022	0.025
Wheat, grain	0.0006	0.0074	0.0087	0.009	0.012
Wheat bran	0.0037	0.0098	0.0118	0.059	0.034
Wheat germ	0.0022	0.0090	0.0103	0.035	0.040
Clover hay	0.0037	0.0088	0.0118	0.059	0.070
Timothy hay	0.0026	0.0105	0.0107	0.042	0.047
Oats, grain	0.0034	0.0110	0.0115	0.055	0.041
Cottonseed meal	0.0048	0.0124	0.0129	0.076	0.023
Rice polish	0.0016	0.0087	0.0097	0.025	0.025
Corn germ	0.0018	0.0097	0.0099	0.029	0.029
Soya beans	0.0010	0.0032	0.0047	0.015	0.024

The results in the first three columns are expressed in grams of phosphorus (element).

The inorganic phosphorus was recovered in five cases, namely, corn meal, timothy hay, oats, cottonseed meal and corn germ. It is interesting in this connection that all five are substances which do not give a large quantity of organic material on extraction. On the other hand, cow peas, wheat, wheat bran, wheat germ, clover hay, rice polish and soya beans are all plant substances which yield a large quantity of soluble organic matter on extraction, which has evidently had its effect in preventing complete precipitation, since the phosphate added was not entirely recovered in these substances.

Hydrolysis has possibly been a factor contributing to the variations in the results by the two methods, especially in the case of cottonseed meal and wheat bran. The higher results in these two substances may indicate the splitting off of inorganic phosphorus from organic compounds. This factor would have considerable bearing on results by the old method, in which extraction and precipitation is made in a water solution. On the other hand, in the new method this factor would not have special significance, since extraction and filtration are made in alcohol and the presence of strong alcohol practically throughout the process tends to prevent enzyme action and bacterial decomposition.

As a factor in causing low results may be mentioned the property of some organic bodies to combine with inorganic salts in water solution and also the property of such bodies of inhibiting the precipitation of phosphorus, either chemically or mechanically. Phytin, proteids and carbohydrates seem to have these properties, some in a marked degree.

The chief considerations which recommend the acid alcohol extraction method may be stated as follows:

(1) Alcohol extraction tends to prevent enzyme and bacterial decomposition of organic phosphorus compounds.

(2) Organic phosphorus compounds in general seem to be practically insoluble in the solvent.

(3) Filtration of the extracts of even the most difficultly filterable materials is very rapid.

(4) Recovery of the alcohol used is possible.

(5) A considerable saving of time over the old method is secured.

(6) Results on all the substances examined seem to be consistent and in all cases added inorganic phosphorus was completely recovered.

The author does not claim that the acid alcohol extraction method gives final and absolute results for inorganic phosphorus in vegetable substances, but hopes that it may be useful in more nearly approximating the truth.

Lack of time has prevented further work on some of the details of the method, such as the influence of a longer time of extraction or a slightly stronger acid, and the substitution of a second acid alcohol separation to take the place of the dilute nitric acid separation in the Erlenmeyer flask, details which might be of considerable interest.

It is also thought that this method might be adapted to the determination of inorganic phosphorus in animal tissues. Tissues dried by vacuum could be extracted by acid alcohol, either before or after ether extraction of fat and lipoid phosphorus, thus determining inorganic phosphorus on the same sample and rendering unnecessary the tedious and, in the case of fresh brain and blood, the somewhat unsatisfactory and difficult method of hot water extraction.

It is the hope of the author that some of these points will be more thoroughly investigated.

The author wishes to express thanks to Dr. E. B. Forbes for his courtesy in making this investigation possible.

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LABORATORY AND PLANT

DESIGN AND EQUIPMENT OF THE CHEMICAL ENGINEERING LABORATORY AT THE UNIVERSITY OF WASHINGTON.

By H. K. BENSON.

Received April 3, 1912.

A description of the new chemistry building of the University of Washington was published some time ago (*J. Am. Chem. Soc.*, **32**, 967). Recently the space set aside for chemical engineering practice has been utilized in the design and equipment of a chemical engineering laboratory of which a brief description may be of interest.

The general plan is shown in the accompanying diagram (Plate I). The room is well lighted and completely fire-proof, since it has a concrete floor, brick walls, and wire-lath-cement ceiling. It is supplied with all the accessory equipment available in the building such as steam, gas, compressed air, etc., and

with the installations named in the description of Plate I.

The function of the laboratory is to offer facilities for the acquirement of familiarity with fundamental processes in chemical manufacture such as distillation, extraction, filtration, desiccation, grinding and pulverization, mixing, calcination, fusion and steam digestion. At the same time it furnishes a workshop for industrial research problems which arise from local conditions.

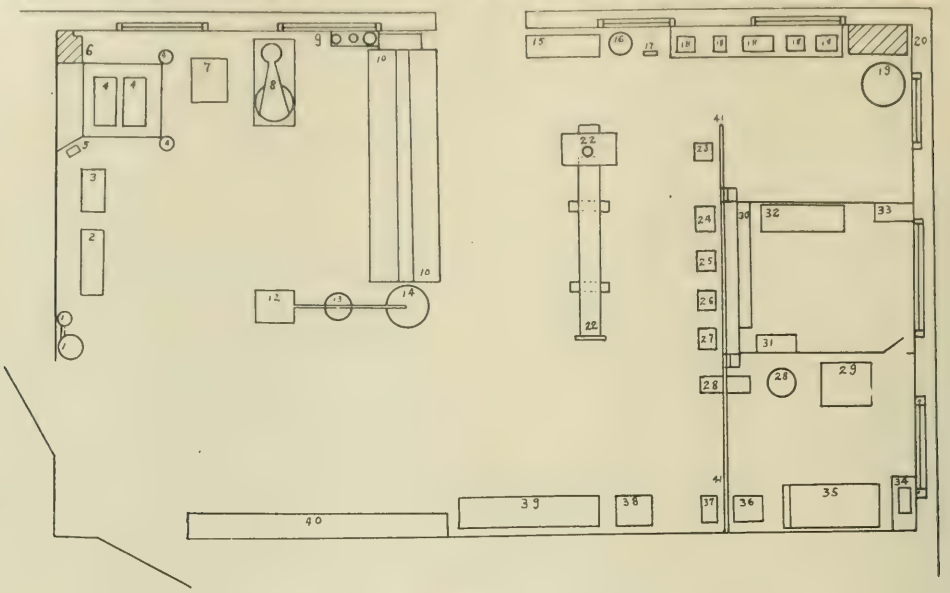

PLATE I.

1. Continuous extraction apparatus.
2. Filter press.
3. Hydraulic press.
4. Wood distillation retort.
5. Drying oven.
6. Flue.
7. Steam superheater.
8. Steam still.
9. Alcohol still.
10. Work table.
12. Vacuum dryer.
13. Condenser.
14. Vacuum still.
15. Sulphurous acid plant.
16. Pulp digester.
17. Fan motor.
18. Heating furnace.
19. Seger furnace.
20. Flue.
22. Rotary cement kiln.
23. Case crusher.
24. Paste mill.
25. Pony mixer.
26. Braun disc. pulverizer.
27. Drug mill.
28. Vacum pump and equalizer.
29. Wood grinder.
30. Shelves.
31. Desk.
32. Balance table.
34. Testing table.
34. Drying closet.
35. Mixing table.
36. 14 H. P. motor.
37. Pebble mill.
38. Moist closet.
39. Storage rack.
40. Lockers.
41. Shafting.

For distillation the laboratory is equipped with a steam still modeled after those used in the turpentine industry: with an electrically heated destructive distillation retort (Fig. 4, Plate II) and with a steam jacketed copper vacuum still (Fig. 1, Plate IV). In the latter the use of steam from a superheater enables a wide range of use in connection with the vacuum pump Fig. 6, Plate III). The extraction of oils by solvents is carried on by means of a continuous extraction apparatus (Fig 1, Plate II) or by pressure in a Boomer and Boschert type of hydraulic press (Fig. 3, Plate II). For filtration and clarification, the Sperry filter press (Fig. 2, Plate II) is used.

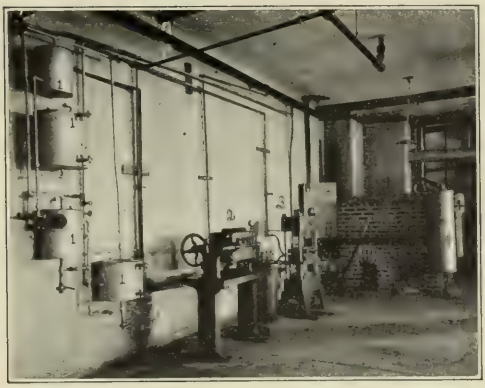

PLATE II.

PLATE III.

The effect of varying pressure on desiccation is illustrated by a Stokes vacuum drier (Fig. 2, Plate IV) which may be subjected to a twenty-four inch vacuum

or a forty-pound air pressure. Grinding machines of various types have been selected. For rock materials, a case jaw crusher (Fig. 1, Plate III) is used and a number of ball and pebble mills in other laboratories are also available. For pigments the Day pony mixer (Fig. 3, Plate III) for mixing and a paste mill (Fig. 2, Plate III) for grinding with oil are employed.

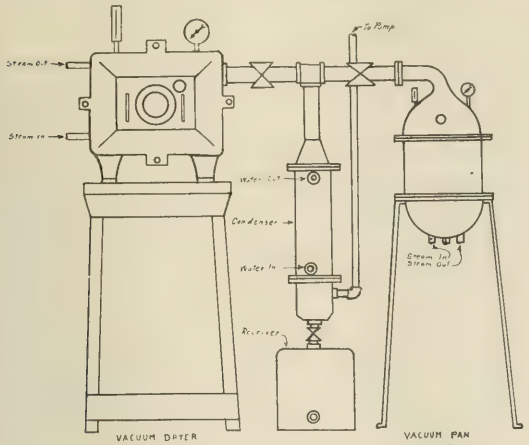

PLATE IV.

For the reduction of wood, roots, bark, etc., to powder form, a Mitts and Merril wood grinder and a Greenbaugh drug mill (Fig. 5, Plate III) have been installed.

A work table for refining operations has been provided with outlets for steam, compressed air, vacuum, gas, water and superheated steam.

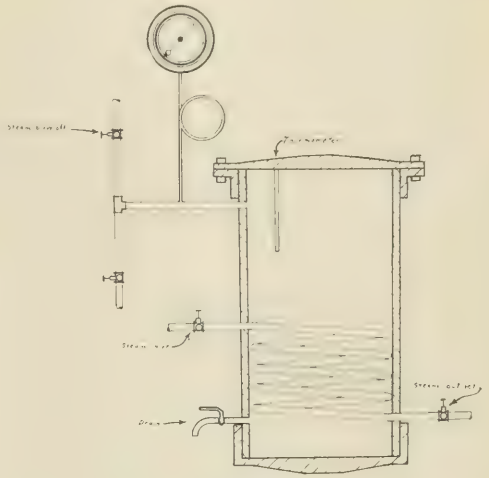

PLATE VI.

From this brief description in connection with diagrams and illustrations it will be seen that stress in chemical engineering education at the University of Washington is laid upon certain fundamental operations, all of which are closely related to the industries now established in the Pacific Northwest.

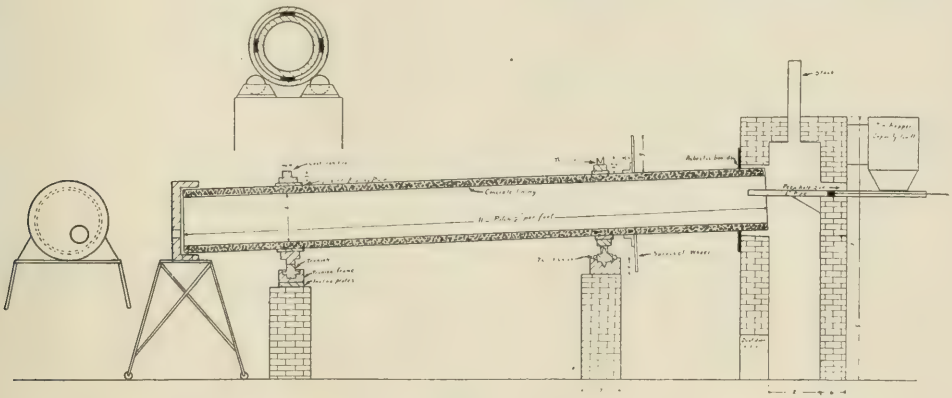

PLATE V.

In the testing of ceramic materials use is made of heating furnaces of the usual type. They are equipped with Case gas burners, a forced draft being supplied by a small motor-driven fan. This equipment also includes a Seger down draft furnace which utilizes preheated air in combustion.

The silicate industry is represented in the installation of cement testing apparatus consisting of moist closet, storage racks, mixing table, tensile strength machine, and in the design of a small rotary kiln equipped with an oil burner (Plate V). For experimental work with lime-silica combinations a small digester (Plate VI) capable of yielding 100 pounds

UNIVERSITY OF WASHINGTON,
SEATTLE.

A NEW APPARATUS FOR THE DETERMINATION OF CARBON DIOXIDE.

By E. W. GAITHER.

Received April 1, 1912.

The apparatus shown in Fig. 2 was designed primarily for the determination of CO_2 in soils by the well known double titration method. It has the advantage over other apparatus used for this determination, in that it does not have to be taken apart for any

...gram involved it is very compact, being set up on a single ring stand and occupies only about 10" to 14" of bench space. There are no very delicate parts; the control of the major operations is centered in a single stopcock, and the adaptability of the absorption process to a wide variety of work. It will stand a vacuum of 70 cm. and is adaptable for either atmospheric pressure or vacuum work.

One chemist can easily operate six apparatus, and by using this number, 36 determinations can be made in an eight-hour day.

After the absorption from one sample is complete the tower can be cut out, another sample started and the CO_2 removed from the apparatus while the first sample is being titrated. When desired, one apparatus can be at atmospheric pressure and another at 70 cm. vacuum at the same time and with the same pump.

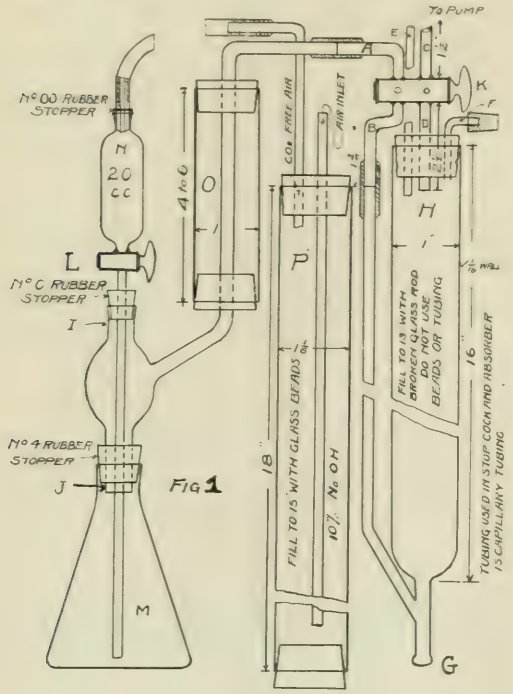

Fig. 1

The entire apparatus can be washed out without taking apart any of the rubber connections. 200 cc. of distilled water will wash out the tower, so that one drop of $N/10$ HCl will more than neutralize the remaining NaOH, if the washing is done properly.

By using 50 cc. of 4 per cent. NaOH, the CO_2 evolved from 1 gram of $CaCO_3$ can be absorbed in 20 minutes, with bubbles passing into absorber at the rate of from 10 to 15 per second.

For ordinary substances that do not foam when boiled, condenser O[1] can be connected direct to flask M through the rubber stopper, thus eliminating the bulb.

[1] Inlet and outlet tubes for cooling this and the corresponding condenser in Fig. 2 are not shown in the drawings

OPERATION.

The apparatus is connected to the suction pipe and a stopcock or screw pinchcock is placed between the suction and absorber H. G, B and D are closed and L opened. A and C are connected by turning stopcock K. Flask M, containing the sample, is connected, the pump started, and the flow of air through P and M regulated by the pinchcock between absorber and suction; while the CO_2 is being driven out of M, introduce the absorbing liquid from a pipette through E and follow it with a little distilled water. Close A, C and L, pour acid into N, connect N to P and open L until equilibrium is reached; connect A,B and D,C, and after adjustments are made apply heat under M and boil for 20 or 30 minutes. Remove heat, close B and D, connecting A and C, cut off suction by means of pinchcock and prepare for next sample. While CO_2 is being exhausted from M, containing second sample, open E and F, draw out absorbed CO_2 through G, connect a funnel to E and pour in water until broken rod in H is covered, draw out through G and repeat the operation; when full, the second time, turn K to connect B and D and allow liquid to rise in B'. When 200 to 250 cc. of water have been passed through H connect A and C. Titrate all or an aliquot of the solution containing the absorbed gas.

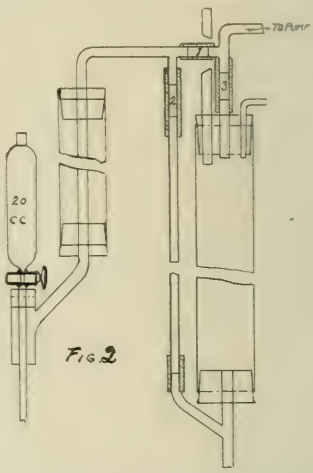

Fig. 2

If the vacuum method[1] is to be used, L is closed and the pinchcock between absorber and suction is opened very slowly until the full vacuum is obtained, then the flow of air is regulated by L. When through digesting, A,B and D,C are closed and suction cut off, L is opened slowly until vacuum in M is relieved, then A,B and D,C are connected slowly until vacuum in H is relieved, other operations being the same as when working at atmospheric pressure.

PRECAUTIONS.

Do not connect A,B and D,C when there is a partial vacuum in M, or liquid will be drawn from H into M. Do not apply heat under M unless suction is previously applied and there is enough vacuum to prevent back pressure, or NaOH solution will be forced out of P through air inlet. Always open F when washing out apparatus or introducing an absorbing liquid. Do not connect B and D when H is full or the liquid will rise in B' and have to be washed out.

The apparatus can be flushed out by removing M

[1] By F. S. Marr, *J. Agr. Science*, **3**, Pt. 2, pp. 156–60.

and N, stoppering J and connecting A,B and D,C, forcing water through I.

Fig. 1 shows a home-made apparatus that gave very satisfactory service until stopcock K was designed to replace pinchcocks 1, 2 and 3.

Hydrogen may be substituted for air by connecting air inlet tube in P to a hydrogen generator.

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Ohio Agricultural Experiment Station,
Wooster.

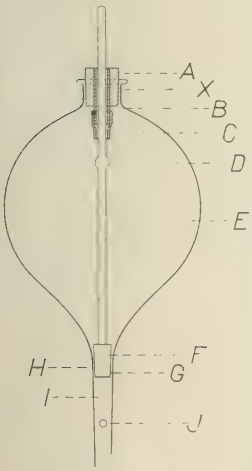
AUTOMATIC FILTER FEED.

By Thos. A. Mitchell.

Received April 18, 1912.

The accompanying diagram shows a device for automatically supplying solution to any laboratory filtering medium where a quantity of liquor, or wash water, is required to be filtered. The apparatus is especially serviceable where it is desired to filter over night.

The main body consists of a pear-shaped funnel of the separatory type, minus the glass stopcock. The neck X is of such size as will take a No. 3 rubber stopper. The outlet I is about 6 cm. long and 1 cm. inside diameter, being slightly enlarged at H to engage the No. 00 rubber stopper G which is attached, as shown, to the glass rod E at F. This glass rod should be of a diameter that will pass freely through the glass tube B 5 mm. in diameter. A nodule is formed by heating as indicated at D.



The upper portion consists of a No. 3 rubber stopper, A, a glass tube, B, 3 cm. long and 5 mm. inside diameter, and a piece of $^3/_{16}$" pure rubber tubing, C, 15 mm. long.

The hole J should be about 4 mm. in diameter and determines the level of the liquor in the filtering apparatus below.

In use, the glass rod E, with stopper G attached, is passed through at X and the stopper G inserted at H. The liquor to be filtered is poured in through X, using the protruding glass rod as a guide for the solution, if it be so desired. After the solution has been added, the parts A-B-C, assembled as a unit, are slipped over the upper end of the glass rod and the rubber stopper A made tight at X.

By quickly lifting the glass rod the nodule D will enter the protruding rubber tube C resulting in an air-tight joint at C and a free passage at H. The amount of liquor passing through H is regulated by the volume of air which enters through the trap J. The hole J is not absolutely essential, but we find it does away with considerable upward suction of the liquor below, thus assuring a better washing of the residues in cases where that is the desired result.

With E-G in position the nodule D should be about 3 cm. below the tubing C.

Chemical Laboratory,
Merrimac Chemical Company,
North Woburn, Massachusetts.

NOTE ON PROTECTORS FOR GLASS STOPCOCKS.[1]

By Walter O. Snelling.

Received May 2, 1912.

Probably every chemist has at some time or other suffered the inconvenience of having a glass cock drop out and break. It is not infrequent for such an accident to result in the loss of the entire apparatus, and at the best there is involved the loss of the time and expense required in sending the parts back to the maker.

Fig. 1

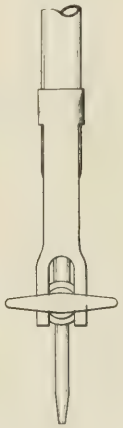


Fig. 2

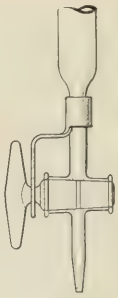


Fig. 3

Some months ago Dr. Charles E. Munroe called my attention to a clip or holder which he had devised, and which was being used by him as an attachment for burets and similar glass apparatus containing stopcocks. The device is simple, easily made, and admirably answers its purpose. It consists of a piece of sheet hard-rubber, so shaped as to encircle some glass part of the apparatus, while a small 2-tined fork passes around the thinnest part of the movable portion of the cock, holding it so securely as to prevent it from dropping out, no matter in what position the apparatus is held, while at the same time allowing perfect freedom of motion of the stopcock, and also enabling the cock to be removed when desired. In Fig. 1 is shown the blank, as cut from sheet rubber, for one form of the Munroe holder, and Fig. 2 shows this form attached to a buret. Ordinary hard rubber sheets of about $^3/_{64}$" thickness is the most convenient material from which to make the blanks. After the blank has been cut it is placed in boiling water for a few minutes to soften, when it may be bent in any desired form, and upon becoming cold will retain whatever form has been thus given it.

Fig. 3 represents another form of the Munroe clip, and one which has also been found to give very satisfactory results. This form is placed permanently upon the apparatus by the blank being bent into

[1] Published by permission of the Director of the U. S. Bureau of Mines.

shape while attached to the buret, both being placed in hot water. The form shown in Fig. 2 can be put on or be taken off the buret at any time, by simply sliding the sleeve along the buret until the tines of the fork are free from the stopcock, and then sliding it down along the tube until it is free.

After I had used the Munroe clip for some time, and had become familiar with the security it affords against the accidental breakage of stopcocks, it occurred to me that for new apparatus, a glass stopcock could be easily constructed which would be quite free from the danger of the cock slipping out. In the preparation of glass stopcocks the cock is always cut off from a longer piece of glass, and it should be a simple and easy matter to leave the glass a little longer than is now usually done, and then after grinding the cock a small groove could be cut in this extended portion.

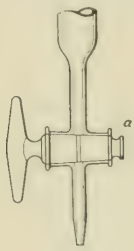


Fig 4

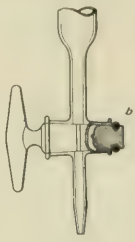


Fig 5

By wrapping a rubber band around in this groove, or attaching a small rubber ring, complete security would be afforded against the accidental loss of the cock. I had some stopcocks prepared as shown in Fig. 4, fitted with a small rubber ring as indicated (partly in section) in Fig. 5. The device affords absolute security against accidental loss of the cock, while at the same time it is nearly invisible, is not in the way of the operator, and can be instantly removed when required. It further serves to keep the cock in place, preventing the loss of fluid which sometimes results from a cock becoming slightly displaced.

The form of holder devised by Dr. Munroe can be readily applied to any type of glass apparatus already constructed, and the form I here suggest can be provided on new apparatus, thus offering for either new or old apparatus a remedy for the the nuisance of broken stopcocks.

BUREAU OF MINES,
WASHINGTON.

ALUNDUM CRUCIBLES IN GRAVIMETRIC ANALYSIS.

By GUILFORD L. SPENCER.

Received April 29, 1912.

The writer tried unsuccessfully to use alundum crucibles in the ordinary Gooch holders, in the gravimetric determination of reducing sugars. The difficulty experienced was in washing the walls of the crucible free of the salts.

It later occurred to me to make the joint at the top of the crucible instead of near the bottom, as in the Gooch method. To do this required a special funnel and a rubber ring, which I procured through Messrs. Eimer & Amend. The arrangement of the apparatus is shown in Fig. 1. The results are satisfactory.

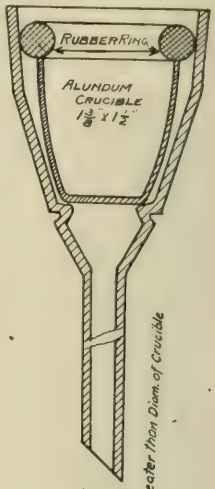


Fig. 1

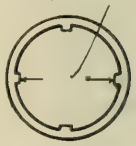


Fig. 2.

The air pressure causes the rubber ring to bear upon the edges of the crucible and against the wall of the funnel, making tight joints. The supporting points in the funnel leave all parts of the crucible accessible for washing.

With the glass funnel, as illustrated, there is some slight difficulty in centering the crucible. I propose to overcome this in the future by the use of a porcelain funnel with centering points, as shown in Fig. 2, or a perforated diaphragm.

I believe that with this arrangement the alundum crucible will be very useful in gravimetric work in agricultural and general laboratories. I expect soon to use it in P_2O_5 determinations. An evident advantage of this type of crucible is the absence of asbestos.

THE CUBAN-AMERICAN SUGAR COMPANY,
NEW YORK AND HAVANA.

ADDRESSES

NATURAL GAS INVESTIGATIONS OF THE BUREAU OF MINES.[1]

By GEORGE A. BURRELL.

Last year at the Pittsburgh convention of the Natural Gas Association, a resolution was passed, asking that the Bureau of Mines assist the natural gas industry in solving problems which arise in the utilization and conservation of natural gas. Although not as active in its investigations as it hopes to be in the future, some progress has been made toward a study of this important fuel.

No attempt has as yet been made toward a complete comparative study of the natural gases from different fields of the country. Some work has been accomplished in that the characteristics of the gas from a few wells in some of the more important fields have been determined, but the Bureau is gathering from many wells in all of the fields a large number of samples, and is submitting them to examination. A bulletin covering this work will be ready for distribution the latter part of the present year. Work already accomplished makes it appear that natural gas consists of paraffin hydrocarbons with nitrogen and carbon dioxide as impurities. The paraffin hydrocarbons may be methane only, or a mixture in which methane and ethane predominate with smaller percentages

[1] Presented at the 7th annual convention of the Natural Gas Association of America, Kansas City, Mo., May 21, 22, 23, by permission from the Director of the Bureau of Mines.

of the higher paraffin hydrocarbons, or in the case of rich casing head gases, a mixture in which ethane and propane predominate. The carbon dioxide may range from a trace, as in the case of the gases of Western Pennsylvania, to as much as 30 per cent., as found in a sample of natural gas obtained from Kings County in Southern California. Nitrogen may occur in quantities ranging from a few tenths of 1 per cent. to as much as 10 or 15 per cent. As an example of an unusual and extreme case, the Bureau found that a natural gas occurring in the State of Washington contained 98 per cent. of nitrogen. In general it may be said that those gases issuing under considerable pressure in the great fields which are providing heat and light for many towns consist of paraffin hydrocarbons in which methane predominates along with smaller quantities of ethane and traces of the still higher paraffins. These gases range in heating value from 900–1100 B. t. u. per cubic foot at 0° C. and 760 mm. pressure with the average more nearly approaching the latter figure. In these days when the heating value is the important factor in determining the usefulness of a gas, such high values are very significant. Contrary to usual text-book information, the Bureau has not been able to detect, in those gases examined, the presence of olefine hydrocarbons, carbon monoxide and hydrogen, although exhaustive tests have been made for these constituents. Natural gases do not lend themselves well to the ordinary examination to which gases are usually submitted. These points will be emphasized in the forthcoming report. It is believed that an analysis of natural gas which shows carbon monoxide, hydrogen and olefine hydrocarbons should be carefully looked into regarding the method employed in examination. The composition of the gas has an important bearing, viewed from several standpoints.

First let it be emphasized that we have, in natural gas, a fuel rich in heat units, non-poisonous, diminishing in quantity and which can be replaced only as Nature sees fit, selling for less than a manufactured product which is not its equal.

From the composition can be determined the relative value of the different gases. It appears that the composition of the gas from a particular well does not vary materially over long periods of time. Sufficient data is not at hand to make this a sweeping statement covering all cases. But in the case of the natural gas supplied to Pittsburgh, the Bureau finds that its composition does not vary appreciably from its composition as determined by F. C. Phillips about 18 years ago. This gas comes from many different wells in the Appalachian fields. As a gas well diminishes in pressure however, the lighter constituents will have been removed and finally, especially where the well is subjected to reduced pressure for the obtaining of gasoline, the heavier paraffin hydrocarbons come off and these when subjected to pressure and low temperature again condense and gasoline is obtained.

Not infrequently, a warning is raised against the introduction of too much carbon monoxide into illuminating gas. Carbon monoxide gives to coal and water gas their powers of asphyxiation, and where the content is high, the intrusion of the gas into a room from a defective connection may result fatally, when we consider that as little as 0.2 or 0.3 per cent. of CO in a room, after a sufficient lapse of time, will bring about unconsciousness and death. Such being the case we are fortunate that natural gas does not contain carbon monoxide.

No one doubts the great importance of the correct determination of the genesis of natural gas and petroleum. Probably the prevailing opinion of the present day has it that natural hydrocarbons are of organic origin, although sufficient proof is not at hand to say that at least some of them may not be of inorganic origin. If of inorganic origin, say by the action of superheated water on the carbides of iron, according to Mendeléeff's hypothesis, then we may be justified in believing that natural gases should contain those constituents that are produced by the decomposition of carbides when the experiments are performed in the laboratory. We could still go farther and believe that the formation of natural gas is continuously taking place, for we are not justified in saying that the carbides have long since been exhausted. Mendeléeff's theory, however, does not stand up in the face of these chemical considerations. The theory that natural hydrocarbons are produced by the destructive distillation of either animal or vegetable matter receives the most support. If such is the case, oil and gas become stored products and are not being continuously generated at the present time. It will be seen from this brief summary that an accurate knowledge of the composition of the different gases becomes essential in order to throw all possible light on the elucidation of the genesis of natural gas. "Where can gas be found?" is the insistent demand of those who already feel the pinch of a diminishing supply. Geologists are in possession of certain facts that help to diminish the risk in drilling wells, but it is only when the drill has made the boring that doubt becomes removed.

Little need be said here about the production of gasoline from natural gas. Suffice to say that by this means a highly useful fuel is being obtained for which there is an ever-increasing demand. The industry rapidly developed from its swaddling clothes so that now it threatens to add considerably to the total quantity of gasoline produced. All natural gases, of course, are not adapted to the manufacture of gasoline. A few wells produce methane as the only hydrocarbon, and for the liquefaction of methane, a pressure of 50 atmospheres at —94° C. is required. Some gases, as Pittsburgh natural gas, some of the Oklahoma gases, and many others contain a large proportion of methane, a smaller proportion of ethane and not nearly enough of the higher paraffin hydrocarbons for the commercial production of gasoline. Other gases, casing head gases, and those drawn from the earth under reduced pressure, may be so rich in the higher paraffin hydrocarbons—butane, pentane, hexane, etc.—that five or more gallons of gasoline per 1000 cubic feet of gas may be extracted. A chemical examination will show what may be expected from a

particular gas in the way of gasoline production with a given plant equipment. The Bureau is making a study of these methods of examination. Perhaps the simplest of the tests applied at the present time consists in the determination of the density of the gas or in shaking the gas with some solvent such as olive oil, cotton seed oil, clairolene oil, etc., in which the higher paraffin hydrocarbons are more soluble than the lower. It was found, for instance, that by shaking 100 cc. of a gas from which a very high yield of gasoline is obtained in 35 cc. of clairolene oil that 80 per cent. of the gas dissolved in the oil. Pittsburgh natural gas lost only 15 per cent. of its volume when treated in the same way. The latter gas cannot be used for the commercial production of gasoline. Pittsburgh natural gas has a density of 0.64 compared to air as 1 at 0° C and 760 mm. pressure while it has been found that natural gases having a density of 0.86 do produce gasoline. The author has found, however, that other gases having the same density and absorption number contain different proportions of the paraffin hydrocarbons so that it cannot be stated that all natural gases having a density of 0.86 will produce gasoline.

The Bureau has issued one publication having to do with the properties of liquefied natural gas. In the production of gasoline a very great waste has occurred, because, in order to make condensates safe for shipment, the lighter products have been allowed to evaporate. The confinement of the material in iron cylinders for use as a bottled gas is now receiving attention. A gas is produced which has a heating value of at least 2200 B. t. u. per cubic foot, and a candle power of about 45 when burned as a naked flame at the rate 5 cubic feet per hour. The use of a mantle will, of course, increase this lighting effect greatly. In order to bring this means of utilizing natural gas to your attention, Mr. I. C. Allen and the writer simply bottled in strong cylinders the condensate obtained by applying a pressure of about 500 lbs. to the square inch and a temperature of 0° C. to crude gas obtained from wells at Follansbee, W. Va. There are some here who could do the same with their casing head gas which is at present going to waste. Once bottled it is only necessary to slightly crack the valve to obtain a supply of true gas.

In experiments conducted at the Bureau, the gas was passed through a small meter, and then burned in a Junker calorimeter. Samples of the gas were also analyzed. By taking the gas from the bottom of the tank its composition remained uniform throughout the test. In the case of the exceedingly rich gas obtained at Follansbee, W. Va., about 50 cubic feet of gas per gallon of liquid were realized. For the better control of the gas as it issued from the bottle, a reducing valve was attached.

The Bureau has, of course, viewed this manner of utilizing natural gas from the standpoint of a purely technical investigation, with no axe to grind, except a step in the conservation of natural resources and believes that some of the gas at present going to waste will eventually be used this way. Millions of people are so situated that gas is not used by them, but if a bottled gas sold at a reasonable price becomes available, the outlet for the material will be large. The Bureau has recently learned that one company is already in the field for the purpose of exploiting the liquid gas. They have named their product "Gasol."

Another means of utilizing natural gas has been tried in that attempts have been made to prepare substitution products, principally chloroform, by the action of chlorine upon methane. Although seemingly difficult to do commercially, one cannot say that such will always be the case. Mention is made of these processes simply as showing that the entire utilization of natural gas may not always be along the line of combustion processes.

Probably in but few instances has surface combustion been applied in this country as yet to the use of natural gas. A 92 per cent. efficiency in the case of gas-fired boilers obtained by Prof. Bone is a noteworthy advance and opens up a wide field for the saving of gas in combustion processes. An installation is not complicated or costly.

In the every-day use of natural gas for domestic purposes, saving may be accomplished if appliances are used which are best suited to the economical combustion of natural gas. Natural gas burners require more air than coal gas burners, and if the same burner regulation is used for natural gas that works well with coal gas, the former is not being completely burned. Some natural gas appliances in use are notoriously inefficient. Progressive gas men should give this question of proper appliances serious consideration. Natural gas is cheap and the tendency may be to use more for any particular purpose than is necessary. A campaign along this line, which would result in a smaller consumption of gas per family, should help remove some of the objection to the inevitable rate rise.

In conclusion, it can be stated that the Bureau of Mines wants to do all it can to conserve the natural gas supplies. Great care must be exercised in the use of deposits which are only bubbles and which when punctured become exhausted. Reckless waste of the gas in the field should be prevented by legislation, and every effort should be made toward the education of all concerned that they may realize the necessity of conserving the supply. It is believed that the Bureau of Mines can do some efficient work along the latter line.

BUREAU OF MINES,
WASHINGTON.

A PLAN FOR THE SUPPORT OF CHEMICAL RESEARCH AND FOR THE BETTER TEACHING OF INDUSTRIAL CHEMISTRY.

By JOHN STEWART.

Received April 19, 1912.

The writer has read with some interest several papers and editorials appearing in the journals of the American Chemical Society during the past year on the subject of the teaching of industrial chemistry and the conservation of chemical research, especially that kind of chemical research which has to do with the applica-

tion of chemistry to the industries. These articles are some of the effects of the increasing competition for the places held by chemists, and the unsatisfactory condition of the industrial chemist in relation to the business of which he is a part. The theme of these articles has been: What ought we to do? What can we do? What should we do to improve the condition of the industrial chemist, to increase his power for rendering useful and efficient service, and through him to benefit the business with which he is connected?

These articles have all had one important point in common, but there the uniformity ends, for each has proposed a different method of solving the problem. Some of these articles have been written by teachers of industrial chemistry who have not had actual, practical experience in the application of chemistry to the industries, if one may judge correctly from the general tone of certain statements made. But it is not intended to offer any criticism of articles heretofore published on this subject, they being in the main thoughtful and ably prepared papers. What we now need is a uniform plan of action. We have a certain unity of purpose. If we can connect with this a plan of solving the problem, which meets with general approval from our Society, or at least with the approval of a good working majority of the Division of Industrial Chemists, and will then work unitedly in accordance with this plan we should be able to accomplish some desirable results.

It is the desire of the writer to aid, if possible, in this movement toward a uniform plan of action. In order to get unity of action it is evident that we must confine ourselves to general principles, and leave details to be solved in accordance with the views of individuals and the necessities of local conditions.

The best proposition that has so far been advanced looking toward the amelioration of the condition of industrial chemistry appeared in the November, 1911, issue of THIS JOURNAL. In that number there appeared a very able editorial entitled "Facilities for Industrial Research." The author of that editorial exhibits thorough, first-hand knowledge of the conditions with which he deals. He advances as a fundamental proposition the following statement: "But there is one field which is richer in the promise of results than all others combined; a field which will yield a more immediate, direct, and tangible return to our own industry, our own profession, and to our own members; and that is in *recognizing the necessity of systematic study of industrial problems and throwing the undivided influence of this Society into the establishment and maintenance of laboratories equipped to answer the eternal questions arising as a result of industrial progress.*"

This quotation contains at least three general principles: 1st, industrial chemical problems require systematic study; 2nd, there should be properly equipped laboratories for such study; 3rd, the American Chemical Society should work as a unit toward the establishment of such laboratories. It is not difficult to conceive that some business men who profit by the application of chemistry to industry would object strenuously to some or all of them. But it is difficult to conceive that any member of the American Chemical Society, who has a sound, thorough training in chemistry, should object to any one of them.

But there must be some other general principles to which a large body of us can agree; otherwise there can not be any further progress toward a solution of the problem. A few of them appear to be of such general acceptability that they will command the support of a large portion, at least, of the American Chemical Society.

In the first place, the establishment of chemical laboratories is generally a business proposition and they are and must be directed and controlled from a business point of view. Of course there is a large portion of the membership of the Society who dislike the term "business," and who prefer to consider their occupation a "profession" rather than a "business." Yet, if the signs of the times are read aright more and more "professional" men are going into business, and "business" is going to be the great "profession" of the not far distant future. In the second place, a business proposition must be a self-supporting proposition, otherwise it sooner or later passes from the sphere of human action. Hence, a chemical research laboratory must be a self-supporting institution.

Some business men who are reaping profits from chemical industries do not act as if they thought chemical research a paying business proposition. They appear to regard the research chemist in much the same way that many research men regard the business man. Both think the other capable of being improved upon to a very marked degree. Some business men of this type even expressly forbid the chemist in their employ to do any experimenting of any kind, and their laboratories are very poorly built, the equipment being scant and the cheapest the market affords, and chemical literature unknown, the laboratories even being without a book of tables for calculations. To this type of business man, chemistry is a two times two are four proposition; every professed chemist is expected to answer off-hand any question concerning the chemistry of any phenomena which may occur. This is not intended as a libel or a joke on the business man but is a clear, cold statement of fact.

Again, some business men recognize that chemical research, if properly directed, may be made a good paying business investment. Some of this type have established research laboratories in connection with their business.

A review of the history of the business man's treatment of the chemist is not flattering to the chemist, but, nevertheless, the business man is slowly but surely being forced (by competition) to change his methods; and the future of industrial chemistry really looks very much brighter than the past. In the judgment of the writer, the business men who manage chemical industries are not going to establish research laboratories in connection with such industries, with any great degree of rapidity. That more of such laboratories will be established is practically certain, but the process will be a slow, hard-fought one.

Now on the other hand, how do we chemists regard research? Do we consider it a paying proposition from the business point of view? Undoubtedly most of us do, but we recognize the profits to be, in many cases very remote; so remote, in fact, that the business man takes no chances on them. And again, we could probably all designate some pieces of work, done usually by "the other fellow" as "research work," which we would hesitate to dignify by that term. Then, too, if we regard research as a business proposition, there is no doubt that it should be directed along the lines of the most immediate and the greatest need. Glancing over *Chemical Abstracts*, we find that a large portion of the space is devoted to abstracts of research papers relating to organic chemistry: out of some 100,000 known compounds, about 75,000 of them are synthetic. Vegetable physiological and animal physiological chemistry are comparatively neglected, yet these are the fields where the natural organic compounds occur. The reason for their comparative neglect is apparently the greater difficulty of research in these lines. We need more and better research into the fundamentals of chemistry, but we also need, and need more immediately and to a greater degree, research into the problems attending the applications of chemistry to industry.

If we admit that the establishment of research laboratories is a business proposition and that the research should be self-supporting, then how is the money for the development and maintenance of the research institution going to be directed into the research treasury. Information of a certain kind is the one valuable asset of a research institution; but knowledge has a peculiar habit of leaking out, so that its benefits get more or less generally diffused among the public without any direct expense to the public. Evidently the public should pay for the development and maintenance of useful research; that is, the State Governments and the General Government should establish and maintain needed research laboratories, and it would seem that the American Chemical Society must necessarily act as a unit toward influencing the public to perform its duty.

But part of the public will object to this kind of procedure, and the strength of this objection is a very serious obstacle in the path of those who favor the move. This difficulty could be partially avoided by the adoption of a plan which appears to the writer to be a better one than that of securing annual or biennial appropriations from Congress or from State legislatures.

Let this society exert its undivided influence to prevail upon Congress and State legislatures to appropriate a sufficient fund for the establishment of research institutions in each State, these research institutions to be established in connection with State universities or agricultural and mechanical colleges, more appropriately with the latter but probably with both. Then let the Government or State aid cease but let the institution remain Government or State property, concerning the administration of which an annual report should be made by those in charge. Let the fund provided be invested in a full fledged manufacturing plant of a kind appropriate to local conditions. Let this plant be managed and operated on a business basis just as if it were the property of a private corporation, but instead of paying dividends on the original investment let the profits be used to maintain needed chemical, physical, and mechanical research laboratories and help support the teaching part of the institution with which it is connected. In this way the taxation of the people for the support of education would be diminished, and their educational facilities improved. It would also enable the people to take an effective part in the prevention of extremely high and extortionate prices for goods, which private corporations are sometimes supposed to levy. The plan would meet with opposition, but most Governmental activities which threaten to reduce *profits*, for the benefit of the people, are antagonized by the business men affected. In this way, the business which benefits by scientific research would pay the expenses of scientific research, which is not altogether true of present conditions.

To illustrate the plan, let me say that the agricultural college of a certain state is located in a rich agricultural region in which several sugar factories are flourishing. If this agricultural college were provided with a million dollar fund, it could purchase, possibly, a sugar factory already in successful operation, or if terms of sale by the owners could not be secured on a satisfactory basis, the college could build a new factory (capable of handling 600 tons of beets per day) at a cost of approximately $350,000.00 to $400,000.00. The balance of the original fund would be required as a working capital. A factory of this capacity would yield an annual profit of about $200,000.00, which could be very appropriately used to pay for the support of education and research.

On this plan, the educational institutions of the country would have the facilities as well as the expert knowledge, both practical and theoretical, to teach successfully industrial chemistry, mechanical engineering and business administration, without "aping" industrial activities on a small scale. No one institution could teach the practice of the whole field of industrial chemistry, but all could teach the general theory as now and each one would be specially prepared to teach one phase of industrial chemistry: in general it is in only one phase of industrial chemistry that the industrial chemist is going to become really expert. Degrees for industrial chemists might be put on the same basis as the Ph.D., or otherwise as the educational institutions should see fit.

Some business men would oppose this plan. But business men are already encroaching upon the field of higher education and research. They are teaching their employees the theory as well as the practice of the particular business in which they are engaged and are at the same time paying the employees wages whereby they are enabled to live while being educated. They are also establishing research laboratories in connection with their business for the study of problems which have to be met and solved. But they are doing this not for the purpose of benefitting their

employees or the general public, but solely for the purpose of increasing *profits*, or saving themselves from being driven out of business by their competitors who are learning cheaper and better ways of doing things, and who are cutting prices as a consequence. It would seem, therefore, that the scientific men could very advantageously to themselves commence to encroach upon the particular field of the business man. When the scientific man gets in control of business, the scientist will fare better in the business world; but only in so far as the scientist gets control, can he hope for much consideration from the business man.

It would seem to the writer also that the American Chemical Society could, very advantageously to itself, endow itself with a fund of say $1,000,000, with which it could go into business for itself. A fund of this size would require about a $200 investment from each member. By proper management the Society could have a considerable annual income to devote to research, the cheapening of publications to the members, or otherwise as desired. There is plenty of business and technical ability in the Society to engineer such a plan to success. The Division of Industrial Chemists is composed of men who are specially fitted for the carrying out of a plan like this in certain fields at least. This kind of a proposition, proposed and carried out by a great body of scientific men, would probably be free from the suspicion that it was only "a stock jobbing proposition." The plan, once in successful operation and fairly administered, would doubtless prove very beneficial to the Society.

LOGAN, UTAH.

CURRENT INDUSTRIAL NEWS

By W. A. HAMOR.

THE MANUFACTURE OF NITRATES FROM THE ATMOSPHERE.

E. K. Scott states (*Nature*, 89, 463) that although the first experimental plant for the manufacture of calcium nitrate by the direct process of Birkeland and Eyde was started only nine years ago, already the Norwegian Hydro-Electric Nitrogen Co., which controls the Birkeland-Eyde patents, has installations aggregating 200,000 horse-power at work and probably by 1916 another 300,000 horse-power will be at work. The other electrically produced nitrogenous manure, calcium cyanamide, is manufactured by a more indirect method invented by Franck and Caro, and its manufacture is not confined to Norway. The following table gives the principal installations, and it may be noted that, although the first one on a commercial scale was erected at Piano d'Orto, in Italy, only eight years ago, there are works in operation, and being built, which by the end of next year will be making calcium cyanamide at the rate of more than a quarter of a million tons per annum.

INSTALLATIONS FOR MANUFACTURE OF CALCIUM CYANAMIDE BY THE FRANCK AND CARO PROCESS.

Name of Company.	Place of installation.	Output in tons per year.
Nitrogen Fertilizers Co. (Northwestern Cyanamide Co.)	Odda, Norway	15,000
Nitrogen Fertilizers Co. (Northwestern Cyanamide Co.)	Alby, Sweden	15,000
Societa Italiana di Prodotti Azotate	Piano d'Orto, Italy	4,000
Societa Italiana per il Carburo di Calcio	Terni, Italy	15,000
Societa Piemontese per il Carburo di Calcio	San Marcel, Italy	3,000
Société Française pour les Produits Azotes	Martigny, Switzerland	7,500
	Notre Dame de Briancon	7,500
Bayerische Stickstoff Werke	Trostberg, Bavaria	15,000
Ost-Deutscher Stickstoff. u. Chemische Werke	Bromberg, Prussia	2,500
A. G. Stickstoffdunger	Knapsack, Germany	18,000
Societa per l'Utilizzazione delle Forze Idrauliche della Dalmazia	Selenico, Dalmatia	4,000
	Dugirat, near Almissa	80,000
Japanese Nitrogen Products Co.	Kinzei, near Osaka	4,000
American Cyanide Co.	Nashville, Tenn.	4,000
	Niagara Falls, N. Y.	12,000

The Nitrogen Fertilizers Co., which owns the Odda and Alby Works, works under license from the Northwestern Cyanamide Co., which company controls England, Norway and Sweden, Belgium, and all the British colonies, protectorates and dependencies, except Egypt and Canada. The Odda plant is being enlarged, and at the beginning of next year will be producing 73,000 tons per annum. In the United States, the American Cyanamide Co. is about to erect a works in Alabama to manufacture 24,000 tons per year.

A PROCESS FOR THE FIXATION OF ATMOSPHERIC NITROGEN.

The Chemical Trade Journal (50, 622) observes that many have assumed a pessimistic attitude on the subject of the fixation of atmospheric nitrogen. This feeling is attributable, in the main, to the fact that the possibilities of the various processes so far devised have been over-popularized, and there can be no doubt as to the ultimate importance of the question. The same *Journal* notes that the price movements of nitrate of soda show evidence rather of market rigging than of any near approach to the exhaustion of the Chilean deposits. Nevertheless, the great German chemical works are keenly alive to the importance of the problem of nitrogen fixation and each is doing something toward its solution; for example, while the Badische Company have reduced their holding in the Norwegian production to nominal proportions, the German patent list bears evidence of the activity of this concern in endeavoring to devise a suitable process.

In the process for the fixation of atmospheric nitrogen described in the *Zentralblatt für de Kunstdungen-Industrie* (see *Chem. Trade J., loc. cit.*), use is made of the fact that the oxides of nitrogen result when mixtures of air with combustible gas are detonated. While this has been known for a long time, the conditions necessary to secure a relatively high yield of nitrous gases has only recently been determined and a commercial plant working on these lines has yet to be erected. The favorable conditions seem to be high pressure, high temperature, and a proportion of oxygen greater than that present in air, that is, an addition of oxygen to the gas mixture is advantageous. It has also been found that previous compression of the gas and air, preferably separately, to 5 atmospheres, notably increases the yield of nitric acid, and that preheating the air and adding 30 per cent. of oxygen have a similar effect. It is said that if these conditions are realized, as much as 12 lbs. of nitric acid per 1,000 cu. ft. of gas may be obtained.

THE CORROSION OF IRON AND STEEL.

The Chemical Engineer (15, 246) gives the following summary

of the results obtained by Friend, Bentley, West and Chappell in their investigations on corrosion of iron and steel, recently presented before the Iron and Steel Institute in London.

Influence of Carbon on Corrodibility.—(*a*) In rolled, normal and annealed steels the corrodibility rises with carbon content to a maximum at saturation point (0.80 per cent. carbon) and falls with further increase of carbon beyond this point. (*b*) In quenched and tempered steels a continuous rise in corrodibility occurs, with increase of carbon within the range investigated (up to 0.96 per cent carbon), no maximum corrodibility at saturation point being found in these steels.

Influence of Treatment on Corrodibility.—Quenching increases the corrodibility to a maximum; annealing tends to reduce it to a minimum; and normalizing gives intermediate values. The influence of tempering varies with the tempering temperature.

Factors Determining Corrodibility.—The electromotive forces between the pearlite and ferrite, and between the components of the pearlite itself, are the principal factors determining the corrodibility of unsaturated pearlitic steels above 0.4 per cent. carbon. In mild structural steels, the galvanic action, due to differences of potential between the constituents, is accompanied by galvanic action betweeen the ferrite crystals themselves. These differences of electro-potential between the ferrite crystals are the result of differences in their orientation. The state of division of the pearlite, and the presence of internal stresses in the steel, may also exert a considerable modifying influence on the foregoing factors. Decarbonization increases the resistance to corrosion. Three per cent. of tungsten produces practically no change in the corrodibility of carbon steels. The influence of time on the rate of corrosion varies with different steels.

USES OF ALUMINUM.

The article by Seligman on "Modern Uses of the Metal Aluminum" (*Science Progress*) calls attention to the applications of the metal in various industries. The sudden demand for aluminum in 1905 was due to the requirements of the motor-car industry; but since additional supplies were not forthcoming, the automobile industry turned to the use of thin steel sheets and frames of special steels, which were often found to be actually lighter than aluminum parts of equal strength. The increased output from 9,000 tons in 1905 to 34,000 tons in 1910 resulted in a fall in price to about one-half, and a certain increase in the earlier demand for aluminum in motor-car work. However, other uses were required to consume the enlarged supply, and in England a very important outlet has resulted from the discovery of methods whereby, with the aid of a special flux, sheets of aluminum may be fused together without the use of any extraneous solder. Vessels made in this way are of special value for chemical industries, and most of all in those involved in the manipulation of food materials. The metal resists corrosion and has the further advantage that it imparts no coloration to the materials in contact with it. In the brewing industry, fermenting tanks up to 30,000 gallons have been constructed, and vessels for fermenting under a pressure of 45 lbs. per sq. in. have been made of 1800 gallons capacity.

In this connection it may be noted that the aluminum companies of France have organized the Southern Aluminum Company, capitalized at $8,000,000.00, and a plant is to be erected at Whitney, N. C., under the direction of the electrometallurgist Héroult.

BRIQUETTING METALLIC WASTE.

A correspondent of the *Scientific American* (**106,** No. 21, 477) states that an Austrian, Arpad Ronay, has recently perfected and patented a process for briquetting metallic wastes without a binder. Ronay applies enormous pressure to the particles, but the application is slow, so that the individual particles may associate and come together to permit of the exclusion of air and water. No binding material whatever is employed, and the process is conducted without heat.

Metallic turnings, chips, filings, etc., are delivered into a large hopper, gravitated into the hydraulic press, and the mass is slowly subjected to increasing pressure. The briquette is then submitted to further compression, up to 2,000 atmospheres.

It is said that briquettes made by the Ronay process from cast iron borings, with a low percentage of phosphorus, can be advantageously substituted for the white iron as used in tempering furnaces; and that Bessemer plants and steel foundries, having Siemens-Martin furnaces using scrap material, find briquettes made from steel and wrought iron turnings a cheaper and more efficient fluxing medium. A number of plants have been erected in Germany for briquetting waste materials by this process, the largest being that built for the Tegel Works of Borsig, which has a capacity of six tons an hour.

THE REVIVAL OF THE KELP INDUSTRY.

Kelp, the ash produced by the incineration of various kinds of *Algae* obtainable in large quantities on the west coasts of Ireland and Scotland, and the coast of Brittany, possesses the following composition: potassium sulphate, 10 to 12 per cent.; potassium chloride, 20 to 25 per cent.; sodium carbonate, 5 per cent.; other sodium and magnesium salts, 15 to 20 per cent.; and insoluble residue, 40 to 50 per cent. One ton is procurable from 20 to 22 tons of wet sea-weed.

It is contended with much show of reason in the *Times Engineering Supplement* for May, 29, 1912, that the manufacture of kelp products would prove to be commercially successful if carried out on a comparatively large scale, with modern chemical engineering methods. The sea-weed should be heated in a retort, as proposed by Stanford, and ammonia and acetic acid recovered from the distillate. Stanford obtained 50 to 80 pounds of ammonium sulphate and 6 to 18 pounds of calcium acetate per ton of air-dried sea-weed. The residual charcoal gives up its soluble salts to hot water and can afterwards be used as fuel. The iodides become concentrated in the mother liquors and may be recovered to the extent of 12 pounds per ton of dry sea-weed in the form of free iodine.

LIGHTING BY NEON TUBES.

According to *Engineering* (**92,** 807), while it has been long known that a vacuum tube charged with neon gives a brilliant light with but little absorption of electric energy, yet there is a progressive absorption of the gas and the light finally extinguished. Claude has described a number of experiments made to overcome this. He found that when the tubes had small electrodes, these heated rapidly nearly to redness, and a metallic deposit formed on the glass in their vicinity. After 88 hours this deposit amounted to 1.6 g. Upon examination, neon was found occluded in the metal. Consequently, as the disappearance of the gas was due to the vaporization of the metal, Claude reasoned that the life of the tube would be lengthened by using larger electrodes, which would keep cooler. He constructed a neon tube, 45 mm. in diameter, with copper electrodes equivalent to a surface of 300 sq. cm. per ampere of current. One of these tubes worked satisfactorily for 210 hours and was then accidentally broken. Therefore, with a tube 6 m. long, with electrodes giving a surface of 500 sq. cm. per ampere, Claude found that the potential difference necessary to maintain the current only changed 4.0 per cent. in 400 hours. The efficiency was excellent, being only 0.8 watt per candle. It is of interest to note that were the energy wholly convertible into that light to which the eye is most sensitive, the output would be 55 candles per watt, according to recent measurements by Buisson and Fabry.

"GRANACIT."

"Granacit" is described by H. Fischer in *Zeitschrift für angewandte Chemie*, **25**, No. 26, 1327. It is a grayish blue, finely grained, very hard and weather durable true granite, of regular crystalline structure. It has a strength of compression of 2,000 kg./sq. cm. and a density of 2.7. Only traces of water are present and the content of pyrite is small; quartz, feldspar and muscovite are the main components. "Granacit" is acted upon by acids only in a dilute and cold condition, while in a concentrated state and hot there is no action, and it is not affected by prolonged subjection to superheated steam. It is used as a special acid-resisting stone, and in the form of towers and columns for distillation, rectification, condensation, absorption, washing and reaction purposes. "Granacit" pressure and vacuum vessels are also on the market. It is especially appropriate as a material for towers for sulphite lye, vessels for acetic acid for white lead factories, phosphoric acid tubes, and in the alkali industry. "Granacit" differs from other granites in that it does not become decomposed when treated with acids. "Granacit" apparatus is being manufactured by a Dresden, Germany, firm.

THE DESTRUCTIVE ACTION OF ACIDS ON CONCRETE.

Neumann (*Tonind. Ztg.*, **36**, 601) records cases in which concrete drains have become damaged, sometimes soon after construction. In every case the destructive action was traced to the presence of acid in the water which had access to the drains, either internally or externally. In one case the swampy soil surrounding the drain contained iron pyrites, and the water became charged with sulphuric acid; in other instances the atmosphere inside the drains became laden with hydrogen sulphide, which underwent slow oxidation to sulphur and sulphuric acid. Sulphuric acid was the most frequent and most powerful destroyer of underground concrete, but such acids as hydrochloric, oleic and acetic, and also carbon dioxide, were found to be almost as harmful. Neumann attributes the destructive action of acids to: (1) The formation of certain calcium and aluminum compounds, accompanied by a large increase in volume; and (2) the formation of soluble compounds (particularly calcium bicarbonate) which go into solution and cause collapse. He gives as remedies: adequate ventilation inside the drains; the use of non-porous clinker poor in lime as a basis for the concrete; and a covering for the exposed surfaces of tar, tar-felt or asphalt.

"IRONIZING," OR "FERROZINCING."

Pure iron, as is well known, is not subject to corrosion to nearly the same extent as steel, and articles made of good wrought iron also suffer less from atmospheric influences than steel. The more impure wrought iron is, the more it approaches steel in the matter of corrosion, and is therefore more in need of protection than pure iron. In view of these facts, states *Engineering* (**93**, 679), Sherard Cowper-Coles has brought out a new process, which he terms "ironizing" or "ferrozincing," as a means of protecting iron and steel from corrosion; this process gives a more permanent protection than zinc coating. The process consists in first coating the iron or steel with pure iron by a special electrolytic method. Pure iron is slightly electropositive to the underlying iron or steel. A zinc, nickel or brass coating is then applied to the pure iron surface, and forms, it is claimed, a more durable coating than zinc applied directly to a wrought-iron or steel surface, since the electrochemical action which is set up when once the zinc is penetrated is reduced.

A NEW PROCESS FOR ELECTRO-ZINCING.

The Engineering Review (**25**, 505) reports that Quentin Marino has devised a method of depositing metals on earthenware and glass by rendering the surface of the article to be coated conductive by "a chemical reaction" which does not involve the application of heat, with the result that the deposited metal is in direct and adhesive contact with the china or glass. The process, as well as the deposition of metals onto iron and steel, consists of combining a reducing agent with the depositing solution, so that all traces of oxide films, etc., are concurrently removed with the deposition of the required metal. It is said that a sound adherent metallic coating may also be produced upon wood and paper; the wood is rendered water and weather proof, while the metallized paper may be employed in making metallic joints. By the process of Marino, it is claimed that 1 to 2 grams of zinc per ampere hour at a pressure of 2 volts may be deposited upon iron or steel.

TEXTILOSE.

Paper (**8**, 18) states that a factory has been erected at Fleissen for the manufacture of "textilose," a substitute for jute. "Textilose" was invented by Emil Claviez, who manufactured it as a substitute for jute and cotton in his spinning and weaving establishment at Adrof, Germany. The invention consists of a material, capable of being spun, made of wood-pulp, cellulose or the like, with which is combined a fleece or nap of textile fibers, such as cotton, wool, linen, jute, or the waste obtained from a carding machine. Claviez claimed that this substance was adapted to all spinning purposes as well as for the manufacture of paper. Uniting the pulp with 10 to 20 per cent. of fleece is effected during the production of the paper on the paper-making machine, preferably at the beginning of the wire cloth, because in this manner the most intimate union is obtained. "Textilose" yarn may be used in the manufacture of bags, linen, carpets, and upholstery fabrics, and may be bleached, dyed and figured.

THE BLEACHING OF LINEN.

In a paper presented before the Manchester Literary and Philosophical Society on April 23, 1912, on the action of bleaching agents on the coloring matter of linen, R. L. Taylor showed that the coloring matter of unbleached linen is quite abnormal with regard to the action of the ordinary bleaching agents upon it, and differs from every other coloring matter. Whereas coloring matters such as indigo, Turkey-red, and the coloring matter of cotton are bleached much more rapidly by free chlorine or hypochlorous acid than by a hypochlorite, with the coloring matter of linen the exact opposite is the case, this being bleached more rapidly by a solution of a hypochlorite. Apparently the maximum bleaching effect on unbleached linen is produced by a solution of a hypochlorite which contains no free alkali, but rather some free chlorine or hypochlorous acid. Excess of alkali retards the bleaching action, just as it does in the case of other coloring matters. The addition of a chloride to the solution sometimes accelerates and sometimes retards the bleaching action (this depending upon the amount of alkali in the solution), instead of, as is the case with other coloring matters, always accelerating it (*Nature*, **89**, 287).

PHOSPHORUS SLAG AS AN INSECTICIDE.

The slag or dross formed in the removal of phosphorus from iron ore has for a long time been used as a fertilizer on account of the phosphorus and lime which it contains. It is pointed out (*Scientific American*, **107**, 6) that recent investigation has shown that the use of this slag is even more profitable than had at first been supposed. The cultivation of the sugar beet in Germany suffers great damage from the plant louse, and the depredations of these insects are also destructive to a large number of plants. J. P. Wagner, a sugar beet expert, recently told the National Society of Agriculture in France of a successful attempt to fight these insects by means of phosphorus slag.

He spread about 1,400 pounds of the slag to the acre on fields that were infested with the plant louse. Not only did this treatment prevent the insects from attacking the leaves, but they were driven away from leaves they had already attacked. On another field the slag was applied in larger quantities, with highly advantageous results. Wagner thinks that the slag forms a thin layer on the leaf, spreading it over the whole surface, and that it is either distasteful or injurious to the insects.

OXYGEN ADDITIONS TO IRON FURNACE BLAST.

It is stated in *The Engineering and Mining Journal* (93, 1180) that according to a report by F. W. Lührmann to the blast-furnace committee of the Verein Deutscher Eisenhüttenleute, the managers of furnaces in Mülheim-Ruhr, in Ougree, and in Kratzwieck, are using oxygen additions in the blast whenever the furnace is working cold. The oxygen is added in small amounts in the form of "Linde air," a liquid-air product containing 50 per cent. of oxygen and 50 per cent. of nitrogen. An installation to furnish 17,500 cu. ft. of oxygen per hour occupies a space of about 125 sq. ft., requires about 800 h. p. to operate it, and costs about $100,000. Lührmann finds that for each per cent. of oxygen added, there is a theoretical rise of 100° F. in blast-furnace temperature. The manufacturers interested state that 1 per cent. of oxygen on a 240-ton furnace costs about $0.50 per ton of pig. If this cost is correct, the method may be found to be of value as an emergency reserve.

NEW COMPOSITE SHEET METALS.

Three new composite sheet metals have recently appeared on the market. *"Hoyt-Silver"* is a britannia metal with an aluminum core, and is said to make silver-plated ware which is lighter, cheaper, stiffer, and stronger than that made from ordinary britannia metal. *"Alumintin"* is sheet aluminum faced upon both sides with pure block tin; it is claimed that it can be electroplated and soldered without difficulty, and that it possesses a density of 3.34. *"White-Copper Stamping Metal"* is sheet aluminum faced on both sides with an antimonial lead alloy; it is reported to be cheaper than either copper or brass, and to be stiffer and harder than antimonial lead. The specific gravity of this composite metal is 5.10. It is easily stamped without annealing and is thought to provide a satisfactory substitute for the usual antimony-lead alloys used in making badges, etc. *The Brass World* (8, 176) states that these products are made by a secret rolling process.

A NEW USE FOR BORON.

E. Weintraub has found that boron can be used for purifying and deoxidizing metallic copper, and has patented his discovery (U. S. Patent 1,023,604). The advantages claimed are that boron possesses a high affinity for oxygen, nitrogen and other gases, but no affinity for copper; and that at the same time it forms an easily fusible slag of boric acid. It is said that if 0.03–0.10 per cent. of boron is added to molten copper, copper castings free from blowholes are obtained and the copper has an electrical conductivity of from 95–98 per cent. Matthiessen standard. The copper also runs freely and fills every portion of the mold. When boron is added, the portion necessary for deoxidizing and purification is consumed, and the excess floats to the top of the fusion as a melted slag. Weintraub states that boron carbide gives equally good results and is much cheaper, while boron suboxide is still more economical.

VANADIUM BABBITT METAL.

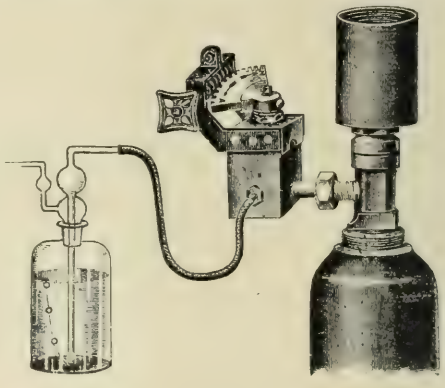
There has appeared on the market a new bearing metal, Vanadium Babbitt, which is made up approximately as follows: tin, 100 parts; antimony, 12 parts; copper and vanadium, 8 parts. The copper and vanadium are melted together, and the fusion is poured into a mixture of molten Straits tin and antimony. The vanadium permits the use of more copper than is generally found in such alloys, gives a denser grain, exceptional tensile and compression strength, and adds 100 per cent. to the life of the bearing.

A NEW VACUUM GAUGE.

According to *Engineering* (93, 539), the ordinary Bourdon type of pressure gauge is not a satisfactory instrument as applied to accurate measurement of vacua. The forces actuating it are then small and what is sometimes termed "sticktion" is accordingly very likely to cause large errors. The ordinary mercury column is also not entirely satisfactory. Water often finds its way to the top of the mercury column, and there is, moreover, some danger of the mercury being accidentally drawn over into the condenser to the ruination of the tubes. A Newcastle-upon-Tyne firm has introduced a gauge under the name of "Kenotometer" to obviate these drawbacks. This new instrument consists of a U-tube provided with a scale. The right-hand leg of this tube is closed at the top forming a barometric vacuum. The left leg of the U-tube is expanded into a vessel of comparatively large diameter. The opening into this limb at the top is through a fine nozzle, upon which, it is claimed, it is practically impossible for mercury to be drawn. This left leg of the U-tube is coupled by a rubber connection to a drying tube, which contains sufficient desiccating material to last for months and is connected up in its turn with the second mercury trap, the top of which is connected to the condenser. The scale with which the instrument is provided is fitted with a rack and pinion adjustment. On the one side it is graduated in 0.1 in. and on the other in percentages of the absolute vacuum.

A NEW FORM OF VALVE FOR GAS CYLINDERS.

A Berlin firm has placed upon the market a new form of valve for cylinders of compressed gases. Since the change in pressure of compressed gases is common, the valve retaining such gases in the ordinary steel cylinders must be constructed strong and solid for the considerable compression which exists. As a certain amount of effort is necessary to open and close, consequently the flow of gas is not constant. A fine and sure regulation of the discharged quantities of gas in a given time is necessary for various purposes. Reducing valves serve only for the regulation of pressure, whereas it is claimed that the new neck valve regulates the amount of issuing gas (German Patent 407,541).



A toothed segment of a wheel of large size, attached to a spindle and operated by a hand-wheel, controls a slight opening of the valve, and hence a very small change in the flow of the gas can be effected.

THE MEASUREMENT OF STEAM CONSUMPTION.

The steam consumed by a turbine or engine can be determined by measuring or weighing the "steam water" or condensate from the surface condenser. A method of doing this (*Industrial Engineering*, 11, 471) is presented in the indicating hot-well, which is attached to the bottom of the condenser, forming a part of the shell. The opening in the bottom of the condenser is constructed so that the condensate drains into the left-hand chamber of the hot-well, and communication from this chamber to the hot-well pump suction is established in the dividing wall. The orifice, polished and finished to insure accuracy of flow, is formed in a brass plate inserted in the partition wall. The indicating gauge is attached to the shell of the hot-well, and ball check valves are provided in each fitting, so that, should the gauge glass break, the flow of air will be prevented and the glass can be conveniently replaced. A gauge glass is also provided for the indication of the height of water in the hot-well suction compartment, in which the water must not be allowed to submerge the orifice. The scale attached to the indicating gauge reads directly in pounds of steam per hour.

A NEW JOINT FOR STEEL PIPE.

The Matheson pipe joint, which was developed for steel or wrought-iron pipe, is similar to the well known bell and spigot joint used with cast-iron pipe. When the pipe is manufactured, one end is expanded into a bell, and around the edge of the bell a reinforcing band of steel is shrunk. The spigot end of the pipe is provided with a slight depression or groove which encircles the pipe near the spigot end. According to *The Engineering and Mining Journal* (93, 1026), in laying the pipe the spigot end is placed in the bell end of the adjacent length of pipe and molten lead is poured into the bell in exactly the same way that the joint of cast-iron bell and spigot pipe is laid. The lead filling may be calked when cool, the reinforcing band adding strength to the bell to resist any tendency to expand as a result of the calking. When the pipe is to be subjected to high pressure, a bolt-flange coupling may be used in conjunction with the lead joint. The advantages claimed are that a strong tight joint is as readily obtained with steel as with cast-iron pipe and that for the same strength steel or wrought-iron pipe is lighter.

NOTES AND CORRESPONDENCE

SEA-WEED, POTASH AND IODINE. A CRITICISM.

In Senate Document No. 190, 62nd Congress, 2nd Session, "Fertilizer Resources of the United States," as well as in an address by F. K. Cameron,[1] sea-weed and especially that of the Pacific coast is mentioned as a possible source of the potash salts used in the United States.

Most of the Senate Document consists of an ordinary description of the stationary growing algae (kelps) and their ecological character. Much space has been given to the species of *fucus* growing in the litoral region. Every expert knows that this species is of no value, as these plants absorb very little valuable material.

The content of inorganic valuable materials in these kelps depends first of all on the physical conditions of their growth. Force of current, temperature, and content of salts are important factors, but other life conditions of the algae also affect their chemical composition. It is of considerable importance whether they are growing near the surface or in deeper water, in comparatively quiet straits or in the breakers of the ocean. The species which, while growing, absorb the most valuable materials are not found in any considerable amounts in the straits or sounds[2] nor in the litoral region, but are abundant out in the ocean, and about the belts of islands, girding the coast, and in these places from the limit of tidewater down to the depth of 20–25 fathoms.

The far more important "Porra" which, until lately, has been given very little consideration, deserves, technically, the greatest attention. A flourishing sea-weed industry on the Pacific coast can be imagined only on the basis of this marine plant. It grows in deeper water and in the open ocean and is consequently richer in valuable materials. It is found in great abundance, is easy to harvest along the coast during fall and winter, and can be worked at proportionately lower cost.

The Senate Document, furthermore, suggests some antiquated methods of burning sea-weed, of preparations of potassium salts, and finally of "Methods of Analyses."

I should advise the use of the "kelpash" and its contents of inorganic valuable materials as the standard scale for the valuation of sea-weed, and not the sea-weed itself. This will simplify transactions between the seller and buyer of kelp or kelpash.

[1] This Journal, 4, 169.

[2] For the last 10 years, I have known the kelp from the interior part of Puget Sound to be of very little, or no value.

Far more interesting are the colored charts, copies of the U. S. Coast Survey Chart. They ought to be combined but they should indicate the special places along the coast, where the "driftkelp" is washed ashore by the stream. As the explorations are limited to the few summer months and as this season mainly comprises all kinds of stationary growing kelp, the useful as well as the useless, we are able to find in the Senate Document little of any importance from which to form any opinion about an eventful lucrative sea-weed industry on the Pacific Coast.

The conclusion drawn from these preliminary explorations is that in the sea-weed of the west coast we have not only a source to furnish all the potash salts consumed in this country but "it means a possible production of potassium chloride about the same as, or even a little larger than, the total production in Germany," and, "taking every consideration and leaning strongly to conservatism, it might be said that it ought to be perfectly practicable to obtain an annual yield of at least a million tons of potassium chloride, worth at present prices, upwards of $30,000,000. The iodine obtainable at the same time should go far toward paying the expenses of harvesting the kelp and extracting the potash."

In the opinion of the writer, $30,000,000 a year, made by potash and perhaps a similar amount or more by iodine extracted from sea-weed on the west coast of the United States, is surely impossible in the light of the following analysis:

1. Is it possible that the Pacific sea-weed can produce sufficient raw material for the production of one million tons of potash salts?

2. Can the potash salts obtained from sea-weed containing a limited quantity of iodine (not more than $^1/_2$ per cent. in the ash of the plant) be furnished at a price similar to that of German potash salt?

To answer the first of these questions, I need only point to the simplest and primitive method of producing (burning) kelpash on the shore. The proposed technical improvements in this process have as yet never been tried practically, and do not promise any such profit as suggested in the published statements.

For the purpose of illustration, I shall use the Nereocystis Lutkeana mentioned in the Senate Document among Dr. J. W. Turrentine's "Analyses of Pacific Kelp," Sample No. 8. This marine plant (a laminaria) belongs to those containing the

largest quantity of both potash and iodine. It is found, as far as known, in the largest quantities at the northern part of the Pacific Coast. The dried plant contains 46.2 per cent. organic matter, 51.3 per cent. soluble salts and 2.5 per cent. ash. Of the soluble salts 2.3 per cent. are actual potash (K_2O) and 0.17 per cent. iodine. The total amount of ash of this plant is 53.8 per cent. The contents of the ash are then 4.2.7 per cent. actual potash (K_2O) corresponding to 67.7 per cent. potassium chloride (KCl) and 0.316 per cent. iodine.

If we take the above-mentioned quantity of ash as a basis, we find that it requires for the production of 1,000,000 tons of potash salts: 0.724,500 tons of wet sea-weed, containing 80 per cent. water, representing 1,948,900 tons of dried sea-weed, producing 1,048,500 tons of ash, representing 1,000,000 tons mixed potash salts.

I presume of course that the whole quantity of soluble salts is extracted as potash salts. This is indeed what is done in practice, as it is quite impossible in a huge production, as the one mentioned, to crystallize the salts singly. Of the potash present, half the quantity will come out as 80–90 per cent. potassium chloride and the other half will consist of a "mixture" of chlorides, carbonates and sulphates, mostly of potassium, sodium and a little part of magnesium containing about 16–20 per cent. actual potash (K_2O), corresponding to the German manure salts, Hartzsalt and Kainit.

For one million tons of potassium chloride, we shall have to multiply the above-mentioned amount of sea-weed and kelpash by two.

I presume that these figures will convince everybody that it is impossible to reach a production of a million tons of potassium chloride on the basis of the sea-weed of the west coast. To furnish entirely the large quantity of potash salts consumed in this country, the United States will have to find other "deposits." It might be of interest to note that the necessary quantity of kelpash containing 0.316 per cent. of iodine, used for the production of a million tons of potash salt, will furnish 7,400,000 lbs. iodine, valued at the present price at $14,000,000 or many times more than the total yearly consumption of the world at present.

Now let us see at what price this kelpash may be produced and how great an army of laborers the production of 1,048,500 tons of kelpash will require.

If the season on the Pacific Coast allows 150 working days for the harvesting and burning of the sea-weed, it will be necessary to produce 7,000 tons of ash a day. If one man produces 200 lbs. of kelpash per day,[1] at a daily wage of $2.00 (on the west coast this is rather low), the ash will cost one cent per lb. or $22.40 per long ton. This is at the present time the average price of kelpash in Scotland and Norway.

The production of 7,000 tons of ash a day for 150 days will require 7,800 men, for only the harvesting, drying and burning of the sea-weed on the shore. For the production of 1,048,500 tons of kelpash twice the number of laborers will be needed. The figures given speak for themselves. I will only add that in practice, conditions will surely be in all respects much less favorable than here anticipated.

The second question, the price of sea-weed potash in competition with German potash, will probably not be any more convincing. Yet this is a more favorable case because we are able to calculate the expense of the production, based on the contents of valuable materials as published in the Senate Document.

Continuing with the favorable marine plant, sample No. 8, Nereocystis Lutkeana, I figured as follows:

[1] A man will have to cut, bring ashore, dry and burn about one ton of wet sea-weed.

Harvesting and burning, per ton ash		$22.40
Freight and other expenses in handling the ash from the coast to the plant, estimated, per ton		2.00
Expenses of production per ton ash:		
Coal	$3.00	
Labor	4.50	
Chemicals	1.00	
Salt bags	2.00	
Commission on the sale of potash and iodine	1.50	
Administration, etc.	1.00	
Interest and depreciation	2.50	
Sundries, taxes, etc.	1.00	16.50
Total cost per ton ash		$40.90
0.316 per cent. iodine = 7.08 lbs. per ton ash at 6 pence per ounce (present price)	14.20	
95.3 per cent. soluble salts, 2134.6 lbs. per ton; of this 1067.3 lbs. are potassium chloride (80–90 per cent. KCl), according to German price $35 per 2000 lbs. net	18.67	
And 1067.3 lbs. are manure salt (20 per cent. K_2O), according to German price $13.30 per 2000 lbs. net	7.09	
Selling price per ton ash		39.96
Loss per ton ash		$ 0.94

Even if all the potash present could be extracted as potassium chloride (which is impossible) it would make only an insignificant improvement on the figures of cost given. The above-mentioned expenses are based on a personal experience of more than 20 years.

In practice the aspect will be far more unfavorable than pointed out above, because I have presumed here that the whole quantity of potash salt as well as iodine could be extracted.

A potash industry on the basis of sea-weed will first and last depend on the content of iodine in the marine plants.

One-tenth of 1 per cent. more or less of this valuable material in the kelpash can change the production from a valueless to a very remunerative business. It is certainly also very important that all of the valuable products in the plants, the organic as well as the inorganic, be utilized.

It is my opinion, nevertheless, that a great and very profitable industry could be founded if the contents of iodine in some of the species of Laminaria on the west coast prove to be satisfactory, but not an industry of any such dimensions as suggested.

Besides the content of iodine, it is of the greatest importance to use the best methods in handling the raw material as well as in the extraction of the products, and furthermore, to utilize to the utmost the valuable materials of the marine plants, both organic and inorganic.

As yet we possess very little of value and very little authentic information to solve the question "Is it possible to build up a *lucrative* industry on the abundant growth of sea-weed at the Pacific Coast?"

HENRIK KNUDSEN.

PHILADELPHIA, PA.

NIGERIAN TIN DEVELOPMENTS.

For some weeks now, great possibilities have been connected with this market, and those who have watched its developments carefully have certainly no reason to complain of the results. It must not be thought that the rise in Nigerian tin shares is devoid of justification. The history of Nigerian tin mining is very modern, although the Niger Company has been shipping tin for some years. The presence of tin in Nigeria was suspected in 1884, but it was not until 1902 that the actual existence of tin in the Bauchi district was discovered. It was in that year that the Niger Company took out a prospecting license over 1,000 square miles of territory. Transport facilities were then, of course, extremely meagre, and it was not until about 1905 that any important deposits were located.

In 1907 the Niger Company stated that it had obtained during the previous fifteen months, roughly, 240 tons of block tin. This was from the Naraguta property which produced on an

average sixteen tons of tin a month. It was not, however, until the latter part of 1909 that the Champion Tin Fields, then known as the Champion Reefs of West Africa, took an active interest in the exploitation of the field..... "The company's first subsidiary, the Tin Fields of Northern Nigeria, was registered in October, 1909; the second, the Nigerian Tin Corporation, was registered on October 14, 1909, and the Naraguta Tin Mines in January, 1910, while the Northern Nigeria (Bauchi) Tin Mines was brought out in February, 1910. The success attending these early concerns had the effect of inducing the more conservative mining houses to take an interest in the mining enterprises of the country, and to-day practically all the largest and most important mining and financial groups are represented by share interests in different companies. Although development was encouraging, operations were naturally hampered by the lack of transport facilities, the roads being mere tracks. After some pressure and a careful inspection of the district, the government consented to provide a railway, which would touch the more important discoveries, and so enable the properties to be developed on a scale adequate to the mineral resources disclosed. This railway will be ready to handle freight about the beginning of April, 1912. Up to the present time the camps on the various properties have had to depend for food, machinery and equipment entirely on loads carried on the heads of the natives, and shipments of tin have been sent down to the coast in the same way. This of course has meant an enormous cost for transportation charges. In fact, freight from the properties to England has been in the neighborhood of £50 to £60 per ton (£1 equals $4.86). The producing companies could, of course, pay even this charge and still make a very substantial profit, but it was quite impossible to get on the grounds the machinery necessary to open up on a reasonable scale the various areas. Naturally, as long as everything had to be carried on the heads of natives, the weights were strictly limited, and unfortunately hydraulic machinery consists of a good deal of dead weight, so that its transportation to the fields, until the railway was within a reasonable distance of the grounds, was out of the question.

"In spite of the difficulties which the companies have experienced, the output has been very encouraging.

"It may be mentioned that for the month of January, 1911, the output was no more than 63 tons of tin, gradually increasing until by the end of the year the total output had been brought up to 1,800 tons of tin oxide, while for the month of January of this year the yield has increased to 204 tons, the yield for the remainder of the year being expected to show the same steady increase, the general estimate being 3,000–5,000 tons.....

"A very important factor in favor of the Nigerian tin district is the fact that the royalty payable to the government is only 5 per cent., whereas in the Straits Settlements it runs up to about 20 per cent.

"As we have mentioned, most of the companies are working tin alluvial either in the beds of the streams themselves or the adjacent banks. The tin deposited is probably brought down in flood time from the tin lodes in the vicinity, as well as being due to the erosion of tin lodes, which are believed to be in the beds of the streams. Until it was possible to get machinery on the grounds the prospecting for tin lodes was not very definitely pursued, but now that transport difficulties are on the verge of being overcome, several discoveries of tin lodes have been reported.

"At the meeting last week of the Anglo-Continental Mines the chairman stated that the lode had been traced about five miles, showing an average width of 30 feet, and assaying about 24 per cent. of metallic tin. If these figures are confirmed by subsequent developments, the value of the find should be nearly £40 per ton of mineralized ground."—*The African World, March 9th.*

But, as the actual values of the tin discoveries in Nigeria have to be proved, it is well to give attention to the warnings given by experts on tin mining, and not be too sanguine and indulge in too inflated anticipations on the basis of first results, although these are undoubtedly highly encouraging. The best results may yet be obtained from alluvial mining in Nigeria, and the wonderful lodes now being discovered may prove, as in other parts of the world, a failure.

W. J. YERBY.

SIERRA LEONE, AFRICA.

THE OIL OF POCHOTE.

The oil of Pochote, "Aceite de Pochote," is the oil derived from the seed of the Pochote plant (Eriodendron occidentale, Eriodendron oesculifolium), a shrub about 5–6 ft. high, that grows in the hot, humid regions of Mexico, in the Philippines and in some other climatologically similar places. For a long time this plant has been cultivated on a small scale by the native Indians who use the oil of the seeds for medicinal purposes. It is only quite recently that larger plantations have been started in an attempt to produce the oil on an industrial scale. The regions where the Pochote plant thrives in Mexico are usually those where cotton and sugar cane are cultivated. A Pochote plantation may, with proper care, last about 5–6 years, at the end of which time it has to be renewed. The renewals or new plantations are usually started with the help of the suckers that come out at the roots of the older plants. It ought to be to the interests of the American oil industry, especially the cotton seed oil industry, to follow the progress of this newly started oil industry, as it is not altogether unlikely that the Pochote oil might to some extent become a rival of the cotton seed oil.

The literature on oils and natural organic substances consulted (Lewkowitsch, Halphen, Sidersky, Abderhalden, Beilstein and others) make no mention whatever of this oil. The oil that might probably be assumed to be its nearest relative is the oil of Kapok, which also is only very scantily described by some of the above mentioned authors.

The following are the results of the examination of this oil that was sent from Oaxaca, southern Mexico.

General observations: At the temperature of 11° C. about half of the volume of the oil separated in the form of a flocculent mass.

The crude is of amber color and has a rather agreeable odor, something of the odor of coco oil. The taste is somewhat bitterish and reminds one of cold extracted cotton seed oil.

Moisture (100–105)	0.59%
Specific gravity 100/100° C.	0.9080
Specific gravity 15.5/15.5° C.	0.9253
Specific gravity 15.5/100° C.	0.8817
Saponification no., Koettstorfer value	192.0
Free fatty acids (as oleic acid)	21.91%
Acid no.	43.58
Iodine no.	85.89
Reichert-Meissl no.	1.5
Hehner no.	95.1
Acetyl no.	42.68
Saponification no. of the acetylated matter	221.34
Crismer test	101.0° C.
Poutet's elaidin test	a pasty foam
Maumené test (according to Archbutt)	88.0
Thermobromic test (according to Hehner-Mitchell)	15.9
Sulfuric acid test	a reddish color
Neutralization no.	175.16
Mean molecular weight	319.70
"Titer" of fatty acids	28.7° C.
Melting point of the insoluble fatty acids	34.0° C.
Iodine no. of the insoluble fatty acids	90.31

From the above results it can be seen that the oil of Pochote might be classed among the semi-drying oils. Its characteristics resemble quite closely those of cotton seed oil. The excessive amount of free fatty acids, as well as the great difference between

the saponification and the neutralization numbers and the high acetyl value, all show the partial decomposition of the sample examined. The bitter taste of the oil is probably also due to this decomposition. Should this decomposition be the result of careless handling, then there is every reason to believe, that, with proper handling and through modern methods of refining, this oil could be made to equal in quality the average cotton seed oil

S. LOMANITZ.

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LECTURES ON THE SMOKE PROBLEM.

In the fall of 1911 the Department of Industrial Research of the University of Pittsburg was provided by a Pittsburg business man with funds for a thorough investigation of the smoke nuisance. At the present time the investigation is being conducted by a staff of twenty-five specialists, of which seven are giving their entire attention to this task. Some of these men are studying the effect of smoke and soot on the atmosphere, on the weather, on plant life, on buildings, and on the public health; some are investigating the economic damage done by smoke and soot; others are making a detailed study of the mechanical devices for preventing or abating smoke; and still others are inquiring into the chemistry and physics of smoke and soot, into the laws concerning the smoke nuisance, and into the history of the subject as a whole.

Recognizing the interest in the smoke problem manifested by a large number of American cities, and in response to inquiries that have been made, the Department announces that the members of its staff are prepared to lecture on the following phases of this problem:

"The Smoke Nuisance" (a general presentation of the main phases of the subject).
"Smoke and the Public Health."
"Smoke and the Cost of Living."
"Smoke and Plant Life."
"Methods and Means of Smoke Abatement."
"The Effect of Smoke on Buildings and Building Materials."
"The Psychology of Smoke."
"The Smoke Nuisance and the Housekeeper."

These lectures will be given any place east of the Mississippi, provided the expenses of the lecturer are assumed.

For further particulars apply to Dr. R. C. Benner, Department of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

DETECTION OF FORMALDEHYDE IN FOODS.

Editor of the Journal of Industrial and Engineering Chemistry:

In view of the introduction of a mixture of nitrite and formaldehyde with the object of masking the reactions of the latter when used as a food preservative, the following experiments may be of interest.

A sample of fresh mixture was divided into four portions and treated as follows:

1. A small amount of commercial formaldehyde solution was added.
2. Small amounts of formaldehyde and sodium nitrite were added.
3. A small amount of sodium nitrite was added.
4. No addition was made.

Portions of each of these were tested with Rimini's test (phenylhydrazin hydrochlorid, sodium nitroprussid and sodium hydroxid). Prompt reactions for formaldehyde were obtained in 1 and 2; negative results in 3 and 4. Other portions of the samples were tested with the well-known test for nitrite (sulfanilic acid and alphanaphthylamin). The response of 2 and 3 was prompt and distinct. No color was produced in 1 and 4. The original mixtures were allowed to stand 24 hours at room temperature and the tests repeated with the same results as obtained at first.

It seems, therefore, easy to unmask nitrite and formaldehyde in the presence of each other.

HENRY LEFFMANN.

PHILADELPHIA, June 8, 1912.

LABORATORY GENERATOR FOR HYDROCHLORIC ACID GAS.

A simpler form of apparatus than the one shown in THIS JOURNAL, 4, 452, was devised by the late Dr. Thomas M. Drown and myself about 1875 and has been used in this laboratory ever since. I am not sure whether it was published. The flask used was half filled with sulfuric acid. The funnel tube with the opening in the end reduced so that a pin will barely pass by, holding the extreme end in the flame of a Bunsen burner, is used for introducing the hydrochloric acid which is dropped in from a burette. A very steady current of gas is obtained.

EDWARD HART.

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EASTON, PA.

BOOK REVIEWS

An Introduction to the Study of Fuel. By F. J. BRISLEE, D.Sc. One of a series of text-books, "Outlines of Industrial Chemistry," edited By GUY D. BENGOUGH, M.A., M.Sc. xx + 269 pp., with 62 illustrations. D. Van Nostrand Co., New York, 1912. Price, $3.00 net.

The preface states that this book is written for the purpose of bridging the gap that exists between the elementary text-books on chemistry and the large treatises dealing with the details of combustion, design of coke ovens, producers, etc.

The general chemical principles of combustion are given, together with calculations of air required for combustion, weight and volume of products of combustion, calculation of combustion temperatures and heat losses.

One chapter is devoted to analysis of fuel and flue gases, and another chapter to calorimetry and determination of the heating value of a fuel. Both of these chapters are largely descriptive and not only lack details, but are devoid of the suggestions and precautions which are so needed by persons just taking up this line of work and for whom the book is intended. The method of coal analysis is not in conformity with good American practice, and only a passing comment is made on the method of securing a representative sample of coal, although the need of it is mentioned elsewhere in the book. Many different fuel calorimeters are described and conclusions drawn to the effect that the constant pressure, bomb, and sodium peroxide types are all equally accurate. The necessity of having calorimeter thermometers accurately calibrated is not so much as mentioned. The heating value of naphthalene is given as 9668 cal., while the U. S. Bureau of Standards give 9610. Considerable trouble has already arisen from the use of the high value of naphthalene instead of the correct one.

The chapter on high temperature measurement is covered in detail with description of many types of pyrometers, together with precautions in regard to their use and method of calibration.

The chapters on natural and artificial solid fuels give the usual characteristic composition of the various fuels, some average analyses of English coals, and a description of the methods of making charcoal and coke.

The chapter on gaseous fuels deals principally with producer and water gas, giving chemical reactions and effects of temperature and pressure. Another chapter briefly describes a few types of producers. The chapter devoted to the theory of the producer gas and water gas reaction is a review of the work of Jüptner and is quite advanced for the class of readers for whom the book is intended.

The subject of explosion and explosion engines is covered from a mathematical and theoretical viewpoint.

The remainder of the book is devoted to air supply, draft measurement, furnace efficiency, fuel economy, heat balances, furnace tests, boiler tests, and liquid fuels. These subjects are treated but briefly and not in such a manner as to enable a beginner to obtain very helpful or practical information. Less space has been devoted to these eight important questions than was given to the one subject of high temperature.

The book is written from a standpoint of English practice and consists largely of descriptive matter together with theoretical and mathematical discussion, without a great deal in the way of practical information or suggestions to guide a beginner in the study of fuel. E. G. BAILEY.

Annual Tables of Constants and Numerical Data, Chemical, Physical and Technological. Vol. 1, year 1910. Published under the patronage of the International Association of Academies by the International Committee appointed by the Seventh Congress of Applied Chemistry which met in London, June, 1909. Quarto. xxx + 727 pp. University of Chicago Press, Chicago, 1912. Price: Bound, $6.00, or $6.54 postage prepaid; Unbound, $5.30, or $5.82 postage prepaid.

The International Committee (1909–1912) is made up of scientists from the 16 principal European countries, Canada, the United States, Argentina, Australia and New Zealand.

The list of compilers of the annual tables includes the names of thirty-one eminent European scientists. The one hundred and four abstractors represent eleven European countries, the United States and Japan. More than three hundred periodicals were examined; the printed list of almost two hundred gave useful data.

The Committee has been subsidized by the French, Dutch, Russian and Swiss Governments and by academies, scientific and industrial societies and private individuals of thirteen European nations, the United States and Japan.

This volume of the Annual Tables includes chapters on the following subjects.

1–4	Coefficient of Compressibility.	281	Osmotic Pressures.
4–30	Density.	282–286	Degree of Association.
31–41	Viscosity.	287–345	Mixtures (Change of State).
42–44	Surface Tension.	346–427	Solubility.
44–48	Coefficients of Expansion.	428–435	Thermochemistry.
48–49	Melting Points.	436–445	Chemical Equilibrium.
50–59	Specific Heats.	445–459	Velocity of Reaction.
59–62	Thermodynamics.	460–490	Conductivity of Electrolytes.
62–79	Vapour Pressures.	491–506	Electromotive Forces.
80	Thermal Conductivity.	507–526	Colloids.
80–82	Radiation.	527–536	Absorption.
83–84	Photometry.	537–588	Crystallography and Mineralogy.
84–85	Reflecting Power.	589–626	Organic Chemistry.
86	Emissive Power.	627–631	Essential Oils.
87–93	Absorption Coefficient.	632–636	Oils, Fats and Waxes.
94–105	Refraction and Dispersion.	637–640	Animal Physiology.
106–188	Spectroscopy.	641–642	Vegetable Physiology.
189–217	Rotary Power.	643–671	Engineering.
218–243	Electricity.	672–699	Metallurgy. I. Mechanical and other Properties of Metals and Alloys.
243–265	Magnetism.	700–721	II. Mechanical Constants.
265–269	Radioactivity.	722–726	Supplement.
269–273	Electrons and Ionisation.		
274–277	Atomic Weights.		
278–279	Atomic Properties.		
280–281	Diffusion.		

Both the Index of Chapters and the Table of Contents are given in French, German, English and Italian; desired data can be easily found by refe ring to the Table of Contents which is to be supplemented in Vol. II (for 1911) by a General Alphabetical Index, and also by a Special Alphabetical Index of all the substances mentioned in Volumes I and II. The four above mentioned languages are paralleled throughout the volume whereever necessary to make clear the data given.

It was anticipated that this volume would appear before the end of the year 1911, but the unforeseen amount of literature to be consulted made this impossible: the Committee hopes, however, to bring out Volume II this year (1912).

The International Committee and their General Secretary, Charles Marie, are certainly to be congratulated on being able to present this substantial, well arranged and clearly printed volume in less than a year after the last 1910 issues reached Paris.

L. E. MARRS.

The Chemistry ot the Radio Elements. By FREDERICK SODDY, F.R.S. Longmans, Green & Co., 1911. Price, $0.90.

This is one of a series of monographs on inorganic and physical chemistry, edited by Alexander Findlay, designed to give summarized accounts of the progress made in recent years along certain of the more actively pursued lines of advance. In no subject could a summarized account be more welcome than in the chemistry of the radioactive elements as the literature on the chemical side of radioactivity is even more widely scattered than that on the physical side. Neither the treatise by Rutherford—now unfortunately becoming out of date—nor the large treatise by Madame Curie, gives a connected account of the chemical properties of the radioactive elements, although a knowledge of these properties is of prime importance to the student of radioactivity. Mr. Soddy is of course one of the best qualified men to write a chemistry of the radio-elements, and into the ninety pages of this book he has condensed in orderly arrangement most that is known of the radioactive elements. One-third of the book is given to a general description of radioactivity—the three types of radiation and methods of measuring, the disintegration theory, and the classification and nomenclature of the elements.

After this introduction the radioactive elements are taken up in the order in which they stand in their respective disintegration series. Immediately under each element is given its period of active life, the type of radiation it emits, the range or absorption coefficient of the radiation, its nearest chemical analogue, and such other data as apply particularly to it. There follows a discussion of other characteristic features and of methods of separation and estimation. The description of methods for the practical estimation of the radium content of ores and solutions will be appreciated by many who would like to make such analyses.

The author brings out clearly the peculiar and very close similarity of chemical behavior of several sets of the radioactive elements, a similarity that has been the cause of no little confusion. The eighty-odd references to original articles are in themselves a very valuable guide. Though the growth of our knowledge of the radioactive elements is so rapid that slight changes could even now be made in the book, it is perfectly safe to say that no student of radioactivity, whether from the chemical or physical side, can afford to be without this little monograph. GEORGE B. PEGRAM.

The Chemistry of the Rubber Industry. By HAROLD E. POTTS, M.Sc., Member International Rubber Testing Committee. One of a series of text-books, "Outlines of Industrial Chemistry," edited by Guy D. Bengough, M.A., M.Sc. viii + 146 pp. D. Van Nostrand Co., New York, 1912. Price, $2.00 net.

This book is appropriately begun with a chapter on Colloidal Chemistry in which the salient features of colloids in general and their bearing on rubber are mentioned.

Chapter II. Raw Rubber and Coagulation. Theories for

presence of latex in the tree, and effect of proteins and resins on quality of rubber are briefly noted. Methods of coagulation and their influence on the quality of the resulting rubber are pointed out. The recent work on discoloration and tackiness is mentioned. The section ends with a brief account of the washing and drying processes.

The next section deals with the rubber hydrocarbon, soluble and insoluble rubber, solutions, the researches of Harries on the constitution of rubber, and its derivatives with various reagents. The chapter is concluded with a complete account of the latest methods for crude rubber analysis.

Chapter III briefly mentions gutta percha and balata.

Chapter IV deals with mixing of rubber. Reclaimed rubber, substitutes, waxes, bitumens, inorganic compounding materials and their functions in rubber compounds are ably discussed.

Chapter V gives a short historical account of the discovery of vulcanization and a brief résumé of the work done on present theories.

Chapter VI. Vulcanized rubber and its analysis are treated in detail.

The author has succeeded in producing a very excellent book, particularly in pointing out to the general reader the significance of chemistry to the rubber industry. W. W. EVANS.

German Varnish Making. By MAX BOTTLER. Authorized Translation with notes on American Varnish and Paint Manufacture by ALVAH HORTON SABIN. Large 12mo., vii + 363 pp., with 55 figures. John Wiley & Sons, New York, 1912. Price, $3.50.

The German methods and ideas of varnish-making as set forth in Prof. Bottler's book on the subject "Die Lack und Firnisfabrikation" are here made available for non-German readers. At the same time a large amount of matter is furnished by the translator so that the original work has been very much amplified in rendering it into English; in fact about half of it appears to be added matter.

Paints are treated of particularly as to their physical constitution and properties, and much of the experimental work recently done upon this subject is described and discussed.

There are two appendices, the first of 96 pages devoted to analytical methods and containing much that is suggestive, and the second of 27 pages containing the formulas of Charles F. Crockett which have a historical interest.

The book, as was perhaps inevitable from its make-up, lacks unity and continuity but contains much valuable matter and will be found useful as a work of reference.

PARKER C. MCILHINEY.

Industrial Organic Chemistry. By SAMUEL P. SADTLER. Fourth edition, 1912, 8vo., 586 pages, 122 figures and 19 diagrams. J. B. Lippincott Co., Philadelphia. Price, $5.00 net.

The striking feature of the fourth edition of this book is the increased amount of space devoted to analytical processes, and it is gratifying to note that many official methods have been included in place of the cut-and-dried methods found in many of the books on analytical chemistry. The idea of furnishing a certain amount of descriptive matter before the analytical methods are given is a happy one, but could be carried even further by showing where the analytical determinations go hand in hand with the manufacturing operations.

The bibliography is very complete and the statistics given should be of value to those interested in any special line of industry.

The subject matter is presented in a very interesting and instructive manner, and for those desiring general information on the branches covered it will be found very helpful.

ALLEN ROGERS.

Vinegars and Catsup, Interpretation of Standards, Analyses, Etc. By R. O. BROOKS. The Spice Mill Publishing Co., 1912.

This small volume of 70 pages is a compilation of articles published by the author in "The Spice Mill" during 1909, and 1910.

Part I gives a brief classification of commercial vinegars; Parts II–V discuss the manufacture and composition of cider vinegar; Part VI describes wine vinegar; Part VII, malt vinegar; Part VIII, spirit and sugar vinegars; and Part IX, tomato catsup.

The author's purpose has been "to acquaint the manufacturing and wholesale trade with a little of the science" of the vinegar and catsup industries and his plan has upon the whole been well carried out. As an elementary treatise upon the technology of vinegar and catsup making, the book contains many facts of interest to the manufacturer as well as to the general reader. C. A. BROWNE.

NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian, Chemists' Club, New York.

Alloy; Metallurgical and Technological Studies in the— Industry. By M. WEIDIG. L. 8vo., pp. 123. Price, $1.50. L. Simion Nachfolger, Berlin. (German.)

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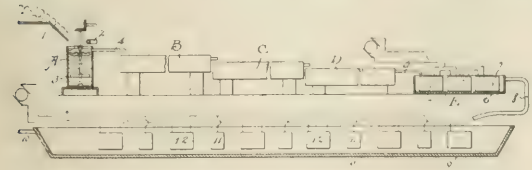
RECENT INVENTIONS

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

METHOD OF SEPARATING AND PURIFYING FULLERS' EARTH AND ANALOGOUS MATERIAL.

U. S. Patent No. 1,024,104, to Charles C. Ruprecht, of Blakely, Alabama.

In many deposits of fullers' earth there is an excess of deleterious material, either organic or mineral. To secure the earth free from such materials, it is found necessary to wash it by mixing thoroughly with water and allowing the mixture of earth and water to pass rather slowly through long tanks or settling



vats in which the excess of sand and other deleterious minerals will be quite completely deposited. It is found, however, that when this settling has been carried to a certain extent, the earth itself will settle with extreme slowness from the water and remains in suspension for weeks or months. Consequently, the mixture after the ordinary washing is very fluid, and the importance of securing the slip in the most dense condition possible to insure rapid recovery, renders it necessary to extract this excess water.

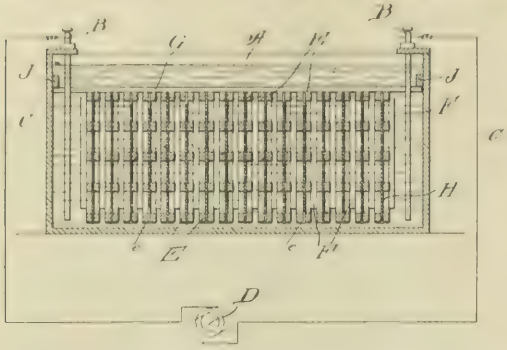
The purpose of this invention is to rapidly and economically precipitate this suspended earth, simultaneously decomposing and removing the organic contaminations. The patentee has discovered that if the water carrying the earth in suspension be electrolyzed, the earth is immediately precipitated and the deposit obtained is so hard that what little remaining water is occluded in its pores may be easily removed by some simple expedient, as by a filter press, centrifugal drier, or evaporation in a suitable kiln.

PROCESS OF CURING HIDES.

U. S. Patent No. 1,025,401, to Frank P. James, of Nashville, Tennessee, assignor to the Electric Meat Curing Company, of Cleveland, Ohio.

In the treatment of hides preparatory to tannnig, it is cus-

tomary, after the hide is removed from the animal, to spread it out, cover it with salt and allow it to stand for several weeks before it is placed in the tanning vat. This curing operation



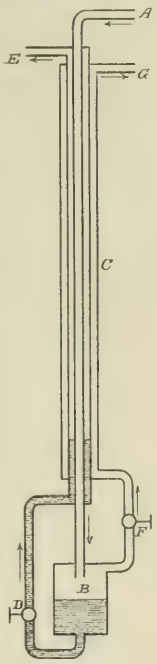
is irregular in its action, some portions of the hide being cured much better than others, and a large amount of the blood is left, which, when the hide is finally converted into leather, is liable to cause it to rot in places.

The patentee has discovered that if the fresh hide is immersed in brine, and a current of electricity passed through the brine and hide, the hide may be perfectly and evenly cured in an extremely short time. The action of the electricity is said to extract the blood from the hide while retaining the gelatin therein.

APPARATUS FOR THE SEPARATION OF HYDROGEN FROM A GASEOUS MIXTURE.

U. S. Patent No. 1,027,862, to Carl von Linde, of Munich, Germany.

There are several processes known for the separation of gas mixtures through liquefaction and fractional distillation, but they are not generally adapted to the separation of gas mixtures containing hydrogen, because the liquefaction of hydrogen can take place only at a temperature so low that all other gases at this temperature exist only in the solid state. The object of the invention is the extraction of hydrogen from gas mixtures, such as illuminating gas or water gas, in such a manner that the less volatile constituents of the gas mixture are condensed through the influence of a reduction of temperature which may also be combined with an increase in pressure. The compression gas mixture enters the apparatus at *A* after it has been previously freed from such constituents or impurities as can bring about stoppages in the liquefying apparatus, *e. g.*, carbonic acid and sulfur compounds. In its passage to the vessel *B*, the gas mixture is reduced to such a temperature in the heat- and temperature-interchanger *C*, that the greater part of the constituents of the gas mixture are liquefied and collect in the vessel *B*. The liquefied portion flows out of this vessel through the expansion mechanism *D* into the interchanger *C*, evaporates and thereby removes heat from the compressed gas mixture flowing through the apparatus. The product of this evaporation, *e. g.*, carbon monoxide,

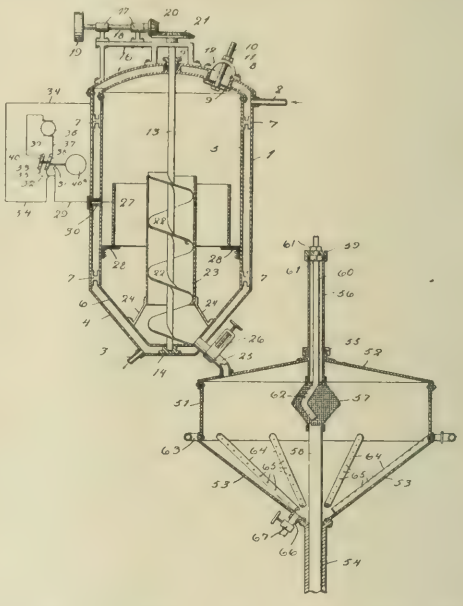


escapes at *F*, after an interchange of temperature with that of the compressed gas mixture passing through the apparatus and can be applied in any manner desired. The portion of the gas mixture which is not liquid (hydrogen and the remaining constituents) after passing through the expansion mechanism *F* flows through the temperature-interchanger *C* in an opposite direction to that of the compressed gas mixture and escapes out of the apparatus *G* at normal temperature.

PROCESS FOR RECLAIMING VULCANIZED-RUBBER WASTE.

U. S. Patent No. 1,024,937, to Chas. S. Heller, of Akron, Ohio, assignor to Moore Architectural and Engineering Co., of Akron, Ohio.

The Heller process of reclaiming rubber, previously patented (Patent No. 978,584), consists in subjecting rubber waste to the action of a heated reclaiming solution and passing a current



of electricity therethrough. Where a dilute alkaline solution was employed as the reclaiming agent, the time of the operation was cut down from about twenty-two hours to ten or eleven hours, by reason of the employment of the electric current. The patentee has now discovered that the time of the operation can be still further curtailed by periodically reversing the direction of flow of the electric current.

PROCESS FOR CONVERTING FATS, OILS, AND FISH-OILS INTO LIKE BODIES OF HIGHER MELTING POINT.

U. S. Patent No. 1,024,758, to Mose Wilbuschewitsch, of Nischninovgorod, Kanavino, Russia.

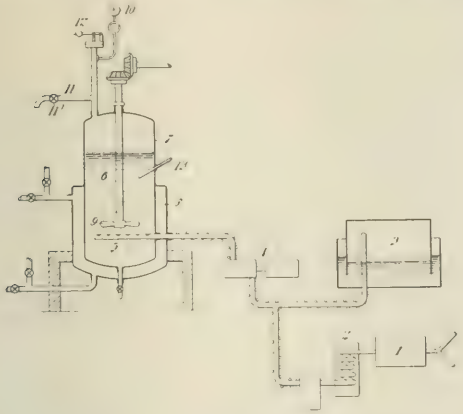
This is a contact process of converting fats, oils, fish oils, and the like into fats of higher melting point, and consists in mixing the fat or oil with the catalyst very intimately and directing against this mixture in a very finely subdivided state in an autoclave under pressure, hydrogen or a gas containing hydrogen. Since in this manner a very intimate contact of the hydrogen with the finely subdivided intimate mixture of fat and catalyst is attained, a comparatively low temperature suffices for the conversion of the fat. The process proceeds in a closed cycle of operations as the catalyst and the hydrogen not consumed are continuously returned to the process.

PROCESS OF FORMING FUSIBLE PHENOL RESINS.

U. S. Patent No. 1,027,794, to Jonas W. Alysworth, of East Orange, New Jersey, assignor of one-half to Frank L. Dyer, of Montclair, New Jersey.

This is a process of forming fusible phenol resins from phenol or cresol by condensation with formaldehyde.

Formaldehyde is generated in the generator 1, and passes through condenser 2, which removes unchanged methylalcohol therefrom, to the gasometer 3, which is provided with an oil

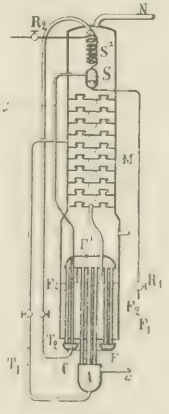


seal and is adapted to be steam-heated. Formaldehyde gas is taken therefrom as desired, by pump 4 and allowed to pass as bubbles from perforated pipe 5 into the liquid phenol 6 in the autoclave 7 which is provided with steam jacket 8, agitator 9, pressure gage 10, vent 11 for the escape of steam when necessary, which is regulated by a valve 11′, and safety valve 12. Provision is made for steam heating the pipes through which the formaldehyde passes, and for passing cool water through steam jacket 8, when the reaction has started, to prevent the temperature from rising above the proper reaction point. This can be regulated by thermometer 13.

METHOD OF EXTRACTING RARE GASES FROM THE AIR.

U. S. Patent No. 1,025,962, to Georges Claude, of Paris, France, assignor to Societe L'Air Liquide, Societe Anonyme Pour L'Etude Et Exploitation Des Procedes Georges Claude of Paris, France.

This invention is a process for the separation of the rarer and less condensable gases as neon and helium, from the atmosphere. It involves the application of well known processes for the liquefaction and separation of the oxygen and nitrogen contained in the air, and modifies the procedure so as to isolate the remaining difficultly condensable gases in the air under treatment.

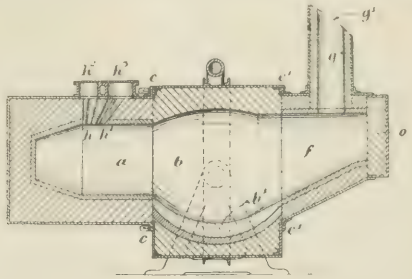


The air under pressure containing the rare gases to be separated is subjected to a process whereby the greater part of the oxygen and of the nitrogen are liquefied, and the remaining unliquefied gas or gases are then submitted to a single or repeated process of liquefaction with backward return, the principles underlying which have been disclosed in the specification of the patentee's prior U. S. Patent No. 924,428. The unliquefied gases, while still under pressure, are brought into direct contact with cold agents and finally with the liquid nitrogen or liquid rich in nitrogen obtained as above. Said nitrogen, being very cold, permits only the uncondensable rare gases, chiefly neon and helium, to preserve their gaseous state.

MANUFACTURE OF STEEL.

U. S. Patent No. 1,024,999, to Tom D. Mackie, of Bowes Park, and George Frederick Forwood, of Limpsfield, England.

According to this method of manufacture, particularly when the production of steel casting is in view, the oxidized metal and slag from the converter (which may be of any known type) are transferred to the hearth of a reverberatory furnace, and, after the removal of the slag, the metal is subjected to the action



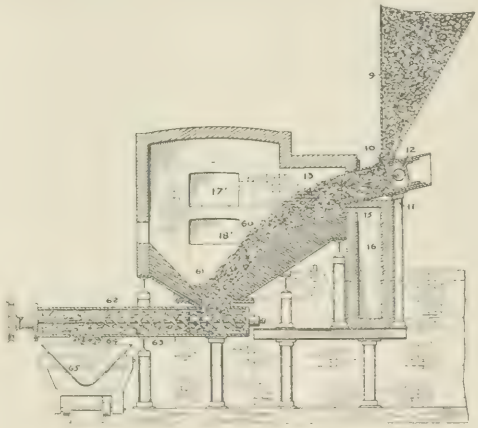
of a reducing gas, such as hydrogen, blue water-gas or the like, with the result that it becomes deoxidized. On reaching the upper portion of the furnace the reducing gas meets with air, becomes ignited and burns, with the effect that the metal is exposed to the heat generated by the combustion, but is protected from its oxidizing influences.

PROCESS AND APPARATUS FOR RECOVERING METALS FROM THEIR ORES.

U. S. Patent No. 1,026,999, to John A. Potter, of Los Angeles, California.

This invention is a process of smelting, roasting, calcining, and sintering all grades of ores.

It consists in heating a series of flues with waste gases from the furnace; then after stopping the waste gas supply, passing fuel gas in the reverse direction, through one of the flues, gas



through another of the flues, and through a third flue reducing gas, discharging the mixture into a reducing chamber, and continuously feeding ore into this reducing chamber. The heat of combustion of the fuel gas assists the reducing gas in melting and reducing the ores. The waste gases so derived are conducted through a similar series of regenerative flues in order to develop the proper temperature and at the proper time the entire cycle is re-reversed.

MARKET REPORT.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF JULY.

ORGANIC CHEMICALS.

Acetanilid	Lb.	20½	@	23
Acetone (drums)	Lb.	17	@	18
Alcohol, grain (188 proof)	Gal.	2.55	@	2.57
Alcohol, wood (95 per cent.)	Gal.	50	@	52
Alcohol, denatured (180 proof)	Gal.	40	@	42
Amyl Acetate	Gal.	2.90	@	3.00
Acetic Acid (28 per cent.)	C.	2.00	@	2.25
Aniline Oil	Lb.	10¾	@	11½
Benzoic Acid	Lb.	23	@	27
Carbon Tetrachloride (drums)	Lb.	11	@	13
Carbon Bisulphide	Lb.	9	@	10
Chloroform	Lb.	20	@	30
Carbolic Acid (drums)	Lb.	15	@	16
Citric Acid (domestic), crystals	Lb.	38½	@	39
Camphor (refined in bulk)	Lb.	44	@	—
Dextrine (imported potato)	Lb.	6	@	7
Dextrine (corn)	C.	2.95	@	3.16
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	18¼	@	19½
Oxalic Acid	Lb.	8⅛	@	8½
Pyrogallic Acid (bulk)	Lb.	1.35	@	1.45
Salicylic Acid	Lb.	32	@	34
Starch (corn)	C.	2.18	@	2.48
Starch (potato)	Lb.	5¼	@	5¾
Tannic Acid (commercial)	Lb.	35	@	35½
Tartaric Acid, crystals	Lb.	30½	@	31

INORGANIC CHEMICALS.

Acetate of Lime (gray)	C.	2.50	@	2.60
Acetate of Lead (brown, broken)	Lb	7¾	@	8
Alum (lump)	C.	1.75	@	2.00
Ammonium Carbonate, domestic	Lb.	8¼	@	8½
Ammonium Chloride, gray	Lb.	6⅛	@	6¼
Aluminum Sulphate	C.	90	@	1.75
Aqua Ammonia (drums) 16°	Lb.	2¼	@	2½
Arsenic, white	Lb.	4	@	4¼
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Barium Chloride	C.	1.40	@	1.55
Barium Nitrate	Lb.	4¾	@	5
Borax, crystals (bags)	Lb.	3½	@	4
Boric Acid, crystals (powd.)	Lb.	7	@	7½
Bromine, bulk	Lb.	25	@	30
Bleaching Powder (35 per cent.)	C.	1.40	@	2.00
Barytes (prime white, foreign)	Ton	18.50	@	22.50
Blue Vitriol	Lb.	5½	@	5¾
Calcium Chloride	C.	65	@	90
Chalk (light precipitated)	Lb.	4½	@	6
China Clay (imported)	Ton	11.50	@	18.00
Feldspar	Ton	7.00	@	9.00
Fuller's Earth, powdered	C.	80	@	85
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1.15	@	1.55
Iodine (resublimed)	Lb.	3.05	@	3.10
Lead Nitrate	Lb.	8⅜	@	8½
Lithium Carbonate	Lb.	65	@	70
Magnesite (raw)	Ton	7.50	@	8.50
Nitric Acid, 36°	Lb.	3⅞	@	4¼
Phosphorus	Lb.	35	@	90
Phosphoric Acid, sp. gr. 1.75	Lb.	22	@	26
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bromide	Lb.	31	@	34
Potassium Permanganate (bulk)	Lb.	9¼	@	9⅞
Potassium Cyanide (bulk) 98–99 per cent.	Lb.	19½	@	21
Potassium Iodide (bulk)	Lb.	2.45	@	2.50
Potassium Chlorate, crystals	Lb.	8¼	@	9½
Potassium Nitrate (crude)	Lb.	4¾	@	5
Potassium Bichromate, 50°	Lb.	6⅞	@	7
Quicksilver	Flask	42.50	@	44.00
Salt Cake (glass-makers')	C.	55	@	65
Silver Nitrate	Oz.	38½	@	40½
Soapstone in bags	Ton	10.00	@	12.00
Sodium Acetate	Lb.	4¼	@	5
Sodium Chlorate	Lb.	8¼	@	9½
Sodium Bicarbonate (English)	Lb.	2¾	@	3
Sodium Bichromate	Lb.	5	@	5¼
Sodium Hydroxide, 60 per cent.	C.	1.70	@	1.75
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent., spot	C.	—	@	2.45
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	6⅞	@	7⅜
Sulphur, Roll	C.	1.85	@	2.15
Sulphur, Flowers (sublimed)	C.	2.20	@	2.60
Sulphuric Acid, 60° B.	C.	85	@	1.00
Talc (American)	Ton	15.00	@	20.00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	13¼	@	13½
Tin Oxide	Lb.	47	@	50
Zinc Chloride (granulated)	Lb.	4¼	@	4½
Zinc Sulphate	Lb.	2¼	@	2½

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	40	@	44
Black Mineral Oil, 29 gravity	Gal.	12	@	12½
Castor Oil (No. 3)	Lb.	9½	@	10½
Ceresin (yellow)	Lb.	9	@	15
Corn Oil	C.	6.00	@	6¼
Cottonseed Oil (crude), f. o. b. mill	Gal.	43	@	47
Cylinder Oil (light, filtered)	Gal.	19½	@	20
Japan Wax	Lb.	10	@	11
Lard Oil (prime winter)	Gal.	85	@	90
Linseed Oil (double-boiled)	Gal.	74	@	76
Paraffine Oil (high viscosity)	Gal.	25½	@	26
Paraffine (crude 120 & 122 m. p.)	Lb.	3	@	3⅜
Rosin Oil (first run)	Gal.	37	@	39
Spindle Oil, No. 1	Gal.	16	@	16½
Sperm Oil (bleached winter) 38°	Gal.	72	@	74
Stearic Acid (double-pressed)	Lb.	9	@	10
Tallow (acidless)	Gal.	62	@	65
Tar Oil (distilled)	Gal.	30	@	31

METALS.

Aluminum (No. 1 ingots)	Lb.	22	@	23
Antimony (Hallet's)	Lb.	7¾	@	8
Bismuth (New York)	Lb.	2.10	@	2.15
Copper (electrolytic)	Lb.	17¼	@	17½
Copper (lake)	Lb.	17⅜	@	17⅝
Lead, N. Y	Lb.	4¾	@	4⅞
Nickel	Lb.	50	@	55
Platinum (refined)	Oz.	46.35	@	47.00
Silver	Oz.	60⅜	@	61⅜
Tin	Lb.	43½	@	45
Zinc	Lb.	7.40	@	7½

FERTILIZER MATERIALS.

Ammonium Sulphate	C.	3.25	@	3.30
Fish Scrap, domestic, dried	Unit	2.45	&	10
Blood, dried	Unit	2.72½	@	2.75
Tankage, high grade	Unit	2.55	&	10
Bone, 4½ & 50, ground, raw	Ton	27.00	@	—
Potassium, "muriate," basis 80 per cent.	Ton	38.55	@	—
Phosphate, acid, 16 per cent.	Ton	7.00	@	7.25
Phosphate rock; f. o. b. mine:				
Florida land pebble 68 per cent.	Ton	3.70	@	3.80
Tennessee, 68–72 per cent.	Ton	4.25	@	4.50
Pyrites, furnace size, imported	Unit	0.13⅛	@	0.13¼
Castor meal	Unit		nominal	
Mowrah meal	Ton	8.50	@	9.00

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume IV | SEPTEMBER, 1912 | No. 9

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Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Penna., under the Act of March 3, 1879.

ESCHENBACH PRINTING COMPANY, EASTON, PENNA.

TABLE OF CONTENTS

EDITORIALS:
- Our Guests ... 634
- Fussy Administration ... 634

ORIGINAL PAPERS:
- Epinephrin from the Whale. By Edward R. Weidlein. 636
- The Chlorides of Carbon as Solvents, I: Carbon Tetrachloride. By Charles Baskerville and H. S. Riedcrer 645
- On the Surface Tension of Silicate and Borosilicate Glasses. By Edwin Ward Tillotson, Jr. ... 651
- The Detection and Determination of Cyanogen and Hydrogen Cyanide. By F. H. Rhodes ... 652
- Rapid and Accurate Methods for Determining Phenol. By L. V. Redman and E. O. Rhodes ... 655
- The Colorimetric Determination of Iron in Lead and its Oxides. By John A. Schaeffer ... 659
- A Rapid Microscopical Method for the Determination of Arsenic, as Orpiment, in Shellac. By Robert Schwarz ... 660
- Some Practical Methods for Testing and Identifying Colors for Printing Inks and Similar P'gments. By Samuel Levinson ... 661
- The Effect of Ignition on the Solubility of Soil Phosphates. By Chas. B. Lipman ... 663
- The Determination of Humus in Hawaiian Soil. By W. P. Kelley and Wm. McGeorge ... 664
- The Composition of Fusel Oil from Beet Molasses. By M. C. Boswell and J. L. Gooderham ... 667
- Difficulties in the Colorimetric Estimation of Vanillin. By W. S. Hubbard ... 669
- A New Colorimetric Method for the Determination of Vanillin in Flavoring Extracts. By Otto Folin and W. Denis ... 670
- Method for Determining Fat in Sugared Evaporated Milk. By F. C. Broeman ... 672

LABORATORY AND PLANT:
- A New Type of Inorganic Filter for Laboratory Purposes. By M. A. Williamson and P. A. Boeck ... 672
- Calculation of Sulphuric Acid Stock by Approximate *vs.* Accurate Methods. A Special Slide Rule for This Purpose. By H. C. Moore ... 677
- A Simple and Inexpensive Conductivity Cell. By Carl A. Nowak ... 679
- Apparatus for Fumeless Kjeldahl Nitrogen Digestion. By A. P. Sy ... 680
- A Simple Method for Purifying Drinking Water. By J. L. Sammis ... 681
- Sampling Conc. By C. W. Kneff ... 682
- A Laboratory Glass-Furnace. By S. R. Scholes ... 683
- The Determination of Carbon in Steel by Direct Combustion in the Newest Form of Shimer Crucible, with the Aid of a Perforated Clay Disc. By Frank O. Kichline ... 683
- A Modified Victor Meyer Apparatus. By Harold Canning Chapin ... 684

ADDRESSES:
- The Analyst versus the Chemist. By J. S. Brogdon ... 684

CURRENT INDUSTRIAL NEWS:
- Factory Inspection ... 686
- Factory Ventilation ... 686
- Mercury Poisoning ... 686
- Specifications for Refractories ... 686
- The Utilization of Sulphite Liquor ... 687
- Italian Shipments of Carbon Disulphide ... 687
- The Condition of the Chilean Saltpeter Industry ... 687
- Methyl Chloride as a Refrigerating Agent ... 687
- Accelerating Paint Drying with Ozonized Air ... 687
- A New Process for Producing Stearic Acid ... 687
- The Rapid Production of Pure Cream of Tartar ... 687
- "Duriron" ... 688
- Lead for Calking Joints ... 688
- "Vanalium" ... 688
- "Argilite" ... 688
- A Water Flow Recorder ... 688
- The Manufacture of Suction Hose ... 688
- Heat Transmission in Vacuum Evaporator Tubes ... 689
- A New Crude Oil Engine ... 689
- A Double-Oiling System Pump ... 689
- Air-Jet Chimney Ventilator ... 689
- The Utilization of Peat ... 689

NOTES AND CORRESPONDENCE:
- Seaweed, Potash and Iodine ... 690
- Ordinary Writing Fluid for Marking Porcelain Crucibles 691
- The Need of Chemical Control in Furnace Operation 691
- The Estimation of Oxygen and Occluded Gases in Copper, Etc.—Author's Note ... 691
- Chemical Industries of Norway ... 691
- Cement Production and Trade of the Far East ... 694
- Sulphur, Pyrite, and Sulphuric Acid ... 695
- Chemical Industry of Germany ... 695
- German Potash and Salt Statistics ... 696
- The Wide Use of Arsenic ... 696
- Swiss Factory Statistics ... 697
- Titanium and Alloys of Steel ... 697
- Good Increase in Platinum Production ... 697
- Paint Production in 1911 ... 697
- Waste in Coke Making ... 697
- Coal Exports in 1911 ... 698

BOOK REVIEWS:
- Correction. Thorpe's Dictionary of Applied Chemistry, A Dictionary of Applied Chemistry; Portland Cement; The Cement Industry in 1911; Practical Chemistry for Engineering Students; Snap Commercial Analysis 698

NEW PUBLICATIONS ... 700

RECENT INVENTIONS ... 701

MARKET REPORT ... 704

EDITORIALS

OUR GUESTS.

As this issue of THIS JOURNAL comes from the press, men from all parts of the world, representing every branch of applied chemistry are assembled in New York in a great International Congress. Individuals, great manufacturing corporations, technical societies and progressive governments are coöperating to make this the greatest event in the history of chemistry. Never before has industry been so willing to acknowledge its debt to chemical science, and the forces behind these international movements will establish its position as the fundamental basis for permanent industrial growth.

Other countries have held these congresses, but American chemists are now for the first time occupying the position of official hosts. We are being honored by the presence of many of the most distinguished men in the profession, and their contributions to the deliberations of the Congress will be of inestimable benefit to the industries. International interchange of ideas has now become a recognized necessity to great industrial progress, and we are proud of this opportunity to render a service in such a cause. Manufacturers are throwing open their plants to inspection and excursions are provided to show the agricultural resources, natural wealth, commercial possibilities and scenic beauty of our country.

The chemists of America feel the sincere solicitude of hosts for the comforts and pleasures of their guests on this auspicious occasion. We hope their visit will be both pleasant and profitable and that they may come again. We wish great benefits to come to the profession itself and to the industries and governments represented as a direct result of the meeting of the Eighth International Congress of Applied Chemistry in America.

FUSSY ADMINISTRATION.

President McKinley handed Colonel Roan a message to carry to Garcia. There were no strings tied to that commission. He had chosen a man of intelligence, resource and ability to do a job and he was willing to let him do it in his own way. This very fact proved that the President was a great executive. He knew how to centralize responsibility and how to hand out a message to a messenger, an art which many men in administrative positions have not yet acquired.

Conversation among employers of men sooner or later drops into a type of experience meeting, for discussing and illustrating the inefficiency of subordinates. Employers never assume any responsibility for the failures of employees, nor do they analyze the causes of shortcomings in their subordinates with a view to seeing how much of the trouble is due to the boss. Many of the failures of men to make good on a given job are due not to a misfit with the job nor to a lack of ordinary ability, but to the man's misfortune in choosing a boss, a condition which he can not always control, but one which he must see and remedy before he will have a chance to succeed.

At a conference in the office of a corporation manager recently, it was decided to send one of the young engineers regularly employed by the company to a point some distance from the main line of travel to take some measurements and get certain simple statistical data. The engineer was called into the office; he quickly caught the points and purpose of the trip, as it was explained to him by the manager; glancing at the clock, he said he would catch the next train. This took about five minutes. The fact that he understood instantly what was to be done, knew what train to take and when to take it, entirely escaped the manager who then spent twenty-five valuable minutes in an unsuccessful attempt to figure out railroad connections from a railroad guide. This bright, well educated young man was then successively told to be sure to order his sleeper tickets at once; to draw what money he needed from the paymaster; to telephone home; to avoid drinking the water because one engineer had been taken sick on a trip similar to this; to be sure to take a note-book but that if he forgot it he could buy one there. At last the young man escaped: the manager mopped his brow and referred at length to the great knowledge of detail he was obliged to carry in his mind in order to run his job.

Subordinates are bound to fail under such conditions as these. Initiative and independence are soon killed, and men and women should not be blamed if they sleep securely at their work in the belief that the "old man" will look out for the details and do the "small thinking" as long as they make a show at the general results. From the manager's standpoint such a system of administration is sure to end in failure. If the business grows, he soon finds his mind so overcharged with fussy details that matters of importance bearing on new problems of development have to be neglected or deferred. Instead of leading and directing the business he becomes a camp follower.

The value of simple mechanical work, whether it be in an office, factory or laboratory, is represented by the market price for the services of a man employed to wield a pick and shovel. A stenographer who simply graphitizes the sounds wafted to her across a flat top desk and later bats them out on her machine without any regard to whether or not they make sense, is worth about one dollar per day—perhaps less, but certainly not more. If she is paid more it is because she is expected to have and use some skill and intelligence in addition to the physical labor of punching keys and making records. It is skill, judgment, intelligence and mental faculties which bring the earning premium to men and women who depend upon industry and business for support. These are the faculties for which the employer pays the premium. If the subordinates do not possess them, they should not be paid the premium; if on the other hand they have the faculties,

latent or developed, they should be required to use them and in this way render services for value received. The employer can find a greater field for his ability and a greater reward for his labor in the consideration of means for developing the intelligence of his employees rather than assuming that part of their work. The problem is one in education—drawing out, developing—and not one in mental "spoon-feeding" to be solved by the circulation of voluminous printed instructions, or by plastering office and works with signs, mottos and "don'ts."

There can be no general rule laid down for developing the responsibility and reliability of subordinates, but it is reasonable to assume that lack of opportunity to exercise these faculties will have much the same effect on their growth that a life of ease and indolence has on the muscles of an athlete. One work manager gave his power-house men much personal instruction for a period of three years on ways and methods of firing and controlling feed water in order to reduce coal consumption. At last in despair at his failure to get results, he gave up this plan, which he was pleased to call education, and adopted in its place a system of paying a bonus on the amount of coal saved below the best previous minimum. The firemen then began to use their own intelligence—the intelligence they had always possessed but never had occasion to exercise while the boss was doing their thinking for them. They soon found that open spots in the grate surface affected their general results as much when the boss was not in sight as when he happened to be present in the boiler room. They became their own bosses and maintained a constant supervision over their own work because they had an objective point, the successful accomplishment of which required an exercise of their own judgment and intelligence. The coal consumption automatically dropped 20 per cent. in two months.

The employer who "butts in" on the prerogatives of his subordinate is not only rendering himself less efficient in the performance of his own work, but is dissipating his resources by paying others for work for which they are employed but which they are not permitted to do. Such employers do not recognize the point at which *directing* ends and *doing* begins.

Probably the most fussy and inefficient form of administration ever invented is the committee system. Committee administration does not exist in approved business organizations, but it appears to be the preferred system in society, public and academic administration.

Questions of business policy, plans for manufacturing development, technical or educational problems all require discussion, consideration and analysis. The experience and knowledge of a number of men working in coöperation is required to determine these matters of general policy. Such questions are properly and efficiently handled by a representative committee selected with a view to reaching a correct and lasting solution. With the solving of these problems and the fixing of a policy for the future administration of the organization their duty should end. It is when this big, unwieldy committee engages in the consideration of nursery problems or attempts to function as an administrative body, that it becomes ridiculous. It has repeatedly been demonstrated that the administrative efficiency of a committee varies inversely as the square of the number of men on the committee. It is well known that business administration is much more efficient and prompt than public, society or academic administration, and the reason is to be found, to a large extent, in the complete freedom of business administration from a triagonal or pentagonal committee attempting to make a job for itself out of the duties of a reliable man. Suppose we take a specific case: An office boy in a well managed business may ask for an increase in salary because he has reasoned out that he is rendering service which will justify it. He goes to the chief clerk who is his immediate superior and is therefore the logical person to control such matters and through such control is enabled to exercise a discipline which puts a premium on efficiency. The chief clerk knows the value of the boy's services, considers all of his arguments and makes a decision one way or the other. If the request is granted, the paymaster is instructed as to the agreement and when it is effective. Total time consumed, about five minutes. Suppose this same boy is working for a committee-mad organization and makes an application for more salary. He is usually advised to "write a letter" covering all points to be considered. The letter is brought up at the next meeting of the board of directors. In order to "save time," after being duly moved, seconded and discussed, the matter is referred to a committee of three or five, to be appointed by the chair, to consider and report at the next meeting on the question of salary for office boy. The committee on office boy's salary is made up of busy men and they find it difficult to get together; it will be a miracle if they do not come in at the next board meeting and report "progress."

In the meantime the boy has become discouraged and has reduced his services to a value comparable with his salary or has obtained a new job at a better salary on account of the knowledge and experience gained while employed by the committee-ridden organization. Running a training school for employees who leave as soon as they have learned enough to be valuable is a discouraging operation at best; such a system of filtration, in which the values all go to the filtrate, will, in an incredibly short time, leave a residual organization which will blunder along with a maximum of inefficiency.

Speed is an important factor in efficient administration. How is the work of a committee going to be expedited? The chairman may call a meeting but the only result is an echo. Men are busy, too busy to be spending their time fussing over insignificant details. We have seen ten ten-thousand-dollar-a-year men sit for hours discussing, considering and acting upon a quantity of insignificant administrative matter which could have been disposed of by one two-thousand-dollar-a-year man in one hour. Such a man, familiar with all questions of policy peculiar to this organiza-

tion, would have acted with even better judgment than the committee because of a more intimate, direct, first-hand knowledge of the facts. The results would have been snappy administration and a living example of practical efficiency to the subordinates—a lesson which could not be drawn from the operations of the hundred-thousand-dollar committee. The committee men themselves often see the ridiculous waste and yet become resigned victims of a system of "fussy" administration which literally oozes with delays, procrastination, irresponsible and inefficient methods.

Most societies and institutions have at least a carload of committee reports which have been made at great expense of time and labor but which have not been read or adopted. Some offices have records—records everywhere—but no obtainable information. In other places the whole organization is busy with the administrative "double pass," where instructions are handed from one subordinate to another and everybody is busy with the system of passing orders along but no one has time to do a job.

Professional men, engineers, chemists and educators might do well to recognize administration as a profession by itself and not a side show to some specialized occupation. As a matter of fact, administrative power is the rarest of all talents and is therefore the best paid profession. We entrust our legal, technical and educational problems to men trained and experienced in their respective specialties. The proper administration of policies so established is equal in importance to, and often more difficult to accomplish than the formulation of the policies themselves. One might properly suggest therefore that the question of efficient administration is important enough to justify careful analysis.

In successful business organizations we find centralized responsibility and power in the hands of a man whose business is administration. Policies are prescribed and commissions are assigned for the purpose of having them executed, and the person who undertakes the work is held responsible for the results. Men of ability and judgment are not converted into errand boys and assigned to duty between the board of directors and the job. Technical questions and questions of policy may be considered and decided by committees but these committees are not "woodenized" by don'ts and limitations. Every man in such an organization believes that the easiest way to dispose of work is to do it. He knows that his boss is waiting for results, not excuses. When he is told to do something, he does not rack his brain for reasons and arguments as to why it should not be done, but puts some intelligence and energy into the matter of doing it. Things are accomplished in an hour which, if undertaken at all in an organization saddled with committee administration or a fussy manager, would take six months.

Since the introduction of laboratory methods of instruction into our educational systems, men trained for numerous activities have been taught to study conditions, observe facts and interpret results. Administrators who apply this training to problems arising in the development of men and women in their organization will have less cause to complain of inefficiency. They will have more people who can carry a message. The elimination of fussy systems of administration will go a long way toward successfully dealing with the human element in efficient management.

ORIGINAL PAPERS

EPINEPHRIN[1] FROM THE WHALE.

By Edward R. Weidlein.

Received June 12, 1912.

The object of this investigation[2] is a study of the ductless glands of deep sea mammals, especially of the whale. The whale is a true mammal, and on account of its size affords a splendid advantage for the study of these glands This paper will be confined entirely to the epinephrin content of the suprarenal glands from the whale and some of the results observed while purifying this product. However, before entering into the subject of epinephrin, it will be best to present something on the morphology and histology of the glands.

The adrenals or suprarenals of the whale are two glandular masses situated above but in close relation with the upper extremity of each kidney, occupying about the same position as the corresponding glands in cattle which they resemble more nearly than those of any other mammal. The left capsule is a little larger than the right, semilunar in form, the right being more nearly triangular. The glands are also larger in the female than in the male whale, but vary in size. The following table gives an average size of the glands found in the animals indicated.

	Glands.	Length. Inches.	Breadth. Inches.	Thickness. Inches.	Weight. Grams.
Fin-back whale, female	Left	9.5	6	1.5	684
	Right	9.5	5.5	1.6	566
Fin-back whale, male	Left	8	5.5	1.1	538
	Right	8	5	2	491
Fin-back whale, calf	Left	7.4	4.1	0.9	280
	Right	6.5	3.2	1.5	264
Sheep		1.0	0.5	0.25	1.18
Hog		1.75	0.5	0.25	2.00
Cattle		2.25	1.5	0.50	12.50

These results show the suprarenal glands of the whale to be about 500 times larger than the glands of sheep and 50 times larger than the glands obtained from cattle.

The glands are composed of a cortex and medulla,

[1] Epinephrin will be used throughout the paper as the standard name for the active principle from the suprarenal glands, as adopted by the Council of Chemistry and Pharmacy of the American Medical Association, in preference to using a commercial or protected name, such as adrenaline, suprarenin, suprarenalin, adrin, supracapsulin, adnephrin and so on. *J. Am. Med. Assn.*, March 25, 1911, p. 910.

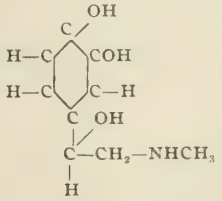
[2] This work was carried out under an Industrial Fellowship established at the University of Kansas by Hon. Walter Roscoe Stubbs, Governor of the State of Kansas, in honor of Dr. Wilfred T. Grenfell, and was known as the Stubbs-Grenfell Fellowship. The Fellowship was extended by a prominent citizen of Pittsburgh.

surrounded by a connective tissue capsule of considerable thickness. The cortex is of a light yellow color, averaging about a quarter of an inch in thickness. It is distinct in lobular division, but does not give as even an appearance as the glands from cattle and sheep. The cortex can readily be separated from the medulla and is oftentimes pulled apart from the medulla. The medulla is of a deep red color varying in thickness, in the right gland from 1–1 3/4 inches, in the left from 3/4–1 inch. The medulla undergoes decomposition very rapidly and can be obtained in good condition from the fresh whales only. The capsule surrounding the gland is of a yellowish-white color and is quite thick. The glands are well supplied with blood vessels, lymph vessels and nerves. The yellow-pigment cells in the medulla are very numerous and well marked.

HISTORY.

Since the extraction of the vaso-constrictor excitant substance of the suprarenal glands from the skin secretions or poison glands of the tropical toad, Bufo Aqua, by Abel,[1] it has given added interest to this field of work, as to the sources of epinephrin. While the discovery of the active principle in the suprarenal glands of the whale is not out of the ordinary or something not to be expected, as compared with Abel's important research, yet it has led to some very interesting results.

The active principle of the suprarenal glands has been a subject of very great importance ever since the valuable discovery of Oliver and Shaefer,[2] that an extract from these glands when injected intravenously would cause a marked rise in the blood pressure. However Vulpian,[3] as early as 1856, observed the characteristic emerald-green and rose-red color which ferric chloride and iodine, respectively, give with epinephrin, while working with the juices from the medulla of the suprarenal gland, thus indicating that there was present in the gland a substance of physiological importance. Abel, Von Fürth and others by very careful and extensive research paved the way for the separation of the active principle, which was accomplished by Takamine in 1901 and named by him "adrenaline." Aldrich advanced this important work by determining the formula for the active principle as ($C_9H_{13}NO_3$). The structural formula generally accepted is orthodihydroxyphenylethanol methylamine:



Comparatively little work had been done on the suprarenal glands until the vaso-constrictor action was made known by Oliver and Shaefer; since that time, however, numerous papers have appeared on the physiology of the glands, together with even more articles on the therapeutic and toxic action of epinephrin. It, therefore, seems preferable to refer only to methods of preparing epinephrin and its physiological results which bear directly on this work. A very complete and excellent bibliography may be obtained by referring to the valuable papers of Abel,[1] Aldrich,[2] Schultz,[3] Vincent,[4] and Shaefer.[5]

The early workers in this field were primarily interested in the therapeutic and toxic action of epinephrin. The preparations used were either water or glycerine solutions from the glands. Of these early workers, Krukenberg[6] and Frankel[7] were instrumental in throwing light on the chemical nature of the active principle, by declaring that it was a pyrocatechin derivative. Fränkel separated what he thought was the active principle and termed it "sphygmogenin." This, however, was later proved to be a mixture. Von Fürth[8] separated the active principle from the glands in the form of an mpure iron compound. Later contributions[9] showed that he separated the active principle by extracting the fresh capsules with slightly acidulated water in the presence of a little zinc dust, concentrating the extract in a vacuum, precipitating the impurities by the use of methyl alcohol and lead acetate, recovering the excess of lead by the use of sulphuric acid, again evaporating the liquid to a small bulk, and precipitating the epinephrin with ammonia. The active principle thus separated was called "suprarenine." Abel[10] first separated the active principle by using benzoyl chloride, one of the benzoyl radicles being retained in a modified form of epinephrin: $C_{17}H_{15}NO_4$ was the formula ascribed to this substance. This compound gave certain of the alkaloidal reactions and was formerly known as epinephrin but as it was stated in the foot-note at the beginning, this name has lately been adopted as the standard name for the active principle from the glands. Abel[11] has since separated epinephrin by using absolute alcohol and trichloracetic acid as the solvent, and precipitating the epinephrin from the concentrated solution by the use of ammonia. In order to distinguish this new substance from his former preparation, he called it epinephrin hydrate. This method increased the yield from 0.2–0.3 per cent. of the moist glands.

The first true separation of the active principle, however, was made by Takamine[12] at the beginning of the year 1901. The method used was in part: to steep the glands in acidulated water, concentrate this solu-

[1] *J. Am. Med. Assn.*, **56**, 1531–6 (May 27, 1911).
[2] *J. Physiology*, **16** (1894); **18**, 230–79 (1895).
[3] *Compt. rend.*, **93**, 663–5 (1856).
[1] *J. Pharm.*, **75**, 301–25 (1903).
[2] *J. Am. Chem. Soc.*, **27**, 1074–91 (1905).
[3] *Bull.* Nos. **55** and **61**, Hyg. Lab., U. S. Pub. Health & Marine Hosp. Serv., Wash.
[4] *Lancet*, **171**, 348–53 (1906).
[5] *Brit. Med. J.*, **1**, 1277–1346 (May 30 and June 6, 1908).
[6] *Virchow's archiv.*, **101**, 542 (1885).
[7] *Wiener Med. Blat.*, **14**, 16 (1896).
[8] *Z. physiol. Chem.*, **24**, 24, 142; **20**, 15 (1898).
[9] *J. pharm. chim.*, [6] **18**, 362; *Pharm. J.*, **24**, 437 (1907).
[10] *The Johns Hopkins Hospital Bulletin*, July, 1897, No. 76; **12**, 339 (1901).
[11] *Ber.*, **36**, 1839–47 (1903). *Am. J. Pharm.*, **75**, 311 (1903).
[12] *Am. J. Pharm.*, **73**, 523–31 (1901).

tion in a vacuum to a small bulk, precipitate the organic protein and inorganic matter by the use of strong ethyl alcohol, reconcentrate and precipitate the epinephrin by the use of ammonia. Aldrich,[1] a little later in the same year, also separated the active principle by using a slightly altered form of Takamine's method. Many new methods have since been worked out to increase the yield and at the same time to improve the quality of the product. Among these might be mentioned a modification which Aldrich[2] made in his own method by using lead acetate as a precipitant. This consists of a precipitation with lead acetate, just after steeping the glands in acidulated water, in order to complete the precipitation of the inert matter, which is removed by filtration. The excess of lead is recovered by passing hydrogen sulphide into the filtrate. The epinephrin is recovered from the filtrate in the same manner as described before. Another method of interest is that of Freund[3] which is the electrolytic reduction of impure solutions of epinephrin or its salts. The electrolytic reduction is by the use of a platinum cathode, a carbon anode and a porous cell as a diaphragm. The solution is made acid and the time required from one to two hours.

Epinephrin has been prepared synthetically through the splendid researches of Dakin, Stolz, Jowett, Böttcher and Pauly. Flächer[4] separated Stolz's synthetic preparation into the *d* and *l*-epinephrin, and showed the *l*-epinephrin to be more effective on the blood pressure and to be identical with natural *l*-epinephrin

Various processes have been suggested for standardizing epinephrin, with the result that three reliable methods have been worked out. These are toxicity, pupil experiments, and blood pressure.

Läwen[5] based a quantitative method on the effect of epinephrin upon the blood vessels of frogs. By this method he could obtain quantitative results and also detect the degree of deterioration of a solution. Strips of muscle were also used in determining the strength of an epinephrin solution.

The toxicity method is of little value, since so many of these experiments were made with solutions from the glands and impure preparations of the active principle, that it is difficult to determine just what is a lethal dose. Schultz[6] has improved this method and has determined the lethal dose to be 0.008 mg. per gram mouse, yet it cannot be used for exact quantitative work.

The dilator mechanism of the frog's eye is quite sensitive to epinephrin. Meltzer[7] was the first to call attention to this method for standardizing such solutions. Auer, Wessely, Ehrmann and Schultz have been instrumental in developing this method of assay. Schultz[8] pointed out that the method devised by Meltzer was good only for qualitative results. He called attention to the various factors which influence the reaction of the iris to adrenaline. A modification of this method was also devised so that the length of the long and short axis of the pupil could be expressed in millimeters, thus eliminating the error that would result by trying to make these observations with the naked eye. These necessary precautions do not eliminate all the sources of error, and not only make the method a very tedious one, but also give unreliable results. There is always present considerable individual variation.

Houghton[1] took advantage of the change of blood pressure produced in the carotid artery by injecting into the femoral vein of an anesthetized animal variable quantities of preparations from the suprarenal glands. In a later paper[2] he proved this method to be the most accurate means for assaying epinephrin. Three solutions of epinephrin of known concentrations were given to an assistant for assay. The unknowns contained 40, 85, and 130 per cent., based on a standard of 100 per cent., and the results reported were 40, 83, and 135 per cent.

Cameron,[3] after trying the various methods for standardizing epinephrin, finally decided on the blood pressure method as being the easiest and most reliable. He was the first to standardize the commercial epinephrin solutions. His method depended upon the antagonistic action between nitrites and epinephrin. He found by using nitroglycerine as a standard, that when 0.5 cc. of 1.5 per cent. 1 : 1000 epinephrin solution was injected along with 1 cc. of solution containing 0.6 mg of nitroglycerine the rise in blood pressure due to epinephrin was almost cut down, and the opposing effect of the nitroglycerine was soon shown by a slight fall and then a return to the normal pressure. After many trials the opposing action between the nitrites and epinephrin was found to be as 80–1. Some of these commercial preparations caused a fall of blood pressure instead of a rise. Papers by Hunt[4] and by Sollman[5] have clearly pointed out the practical necessity for testing the various commercial products from the suprarenal glands. They further show the great value of the blood pressure method in making these determinations. In order to more clearly show the accuracy of this method, Abel calculated that 1 gram of the dried gland from the cattle should contain 0.018 gram of epinephrin and should yield 18 cc. of a solution corresponding to 1 : 1000 of the active principle. Hunt found that it yielded 15 cc. of such a solution and called attention to the fact that the glands were not completely exhausted.

Schultz[6] has more clearly pointed out the necessity of knowing the degree of effectiveness of an epinephrin solution. He also emphasized the fact that a pure epinephrin base furnishes a reliable standard in

[1] *Am. J. Physiol.*, **5**, 457 (1901).
[2] *J. Am. Chem. Soc.*, **27**, 1077 (1905).
[3] *Chem. News*, Feb. 19, 1909.
[4] *Z. physiol. Chem.*, **58**, 185–8–9–94 (1908).
[5] *Arch. exp. Path. Pharm.*, **51**, 413–31 (1903).
[6] *Bull.* **55**, 36, Hyg. Lab., U. S. Pub. Health & Marine Hosp. Serv., Wash.
[7] *Am. J. Physiol.*, **11**, 28–51 (1904).
[8] *Bull.* **55**, 23, Hyg. Lab., U. S. Pub. Health & Marine Hosp. Serv., Wash.

[1] *J. Pharm.*, **73**, 531–5 (1901).
[2] *J. Am. Med. Assn.*, **38**, 150–3 (1902).
[3] *Proc. Roy. Soc. Edinburgh*, **26**, 157–71 (1906).
[4] *J. Am. Med. Assn.*, **47**, 790–2 (1906).
[5] *Ibid.*, **47**, 792 (1906).
[6] *Bull.* **61**, 7–10, Hyg. Lab., U. S. Pub. Health & Marine Hosp. Serv., Wash.

assaying vaso-constrictor substances. The blood pressure method is used and the efficiency expressed in terms of pure epinephrin base. The relative activity is calculated by the following equation:

$$\frac{a \text{ epinephrin base}}{y \text{ vaso-constrictor excitant}} = \text{relative activity},$$

in which a = grams of base in 1 cc. of solution and y the unknown vaso-constrictor excitant.

In this method of standardization,[1] he clearly points out the advantages of different anesthetics and shows that ether for cats, with only enough curare to render it free from muscle tremors, yields the best results. He has standardized all synthetic preparations against the natural *l*-epinephrin and also all commercial preparations against the pure epinephrin base. Three out of seven different brands of epinephrin were found to compare with the standard. The other solutions varied from 3.71 to 71 per cent. of the required activity. These results are given in the following table:[2]

Laboratory number of solution.	Commercial name.	Precipitate present.	Relative physiological activity expressed in percentage of A.
A[1]	Epinephrin	none	100.00
Bd[2]	Adnephrin	none	50.00
Bm[3]	Adnephrin	none	50.00
Cd	Adrenalin	none	100.00
Cm	Adrenalin	none	100.00
Dd	Adrin	none	50.00
Dm	Adrin	abundant	3.75
Em	Caprenalin	abundant	25.00
Fd	Supracapsulin	none	100.00
Fm	Supracapsulin	trace	100.00
Gd	Suprarenalin	none	66.71
Gm	Suprarenalin	none	66.66
Hd	Suprarenin synthetic	trace	50.00
Hm	Suprarenin synthetic	some	50.00

[1] Solution A made up on morning of experiment from a pure sample of natural base, the optical activity of which is $\frac{26.4^0}{D} = 5340^0$.

[2] Series "d" bought directly from manufacturer or from their agents.

[3] Series "m" bought on the open market from a reliable druggist.

Epinephrin solutions deteriorate very rapidly, especially when exposed to the air or if kept in partially filled containers. Schultz has also made a careful examination into this phase of the subject and has summarized his preliminary results in the preceding table.

CHANGES IN PHYSIOLOGICAL ACTIVITY UNDERGONE, IN THE COURSE OF TEN DAYS, BY 1–10,000 SOLUTIONS OF COMMERCIAL EPINEPHRIN SOLUTIONS.[3]

Laboratory number of solution.	Commercial name.	Rise of blood-pressure caused by 1 cc. injection of a 1–10,000 solution. Oct. 29 (fresh).[1] Mm.	Oct. 29 (old).[2] Mm.
Bd[3]	Adnephrin	74.2	69.2
Bm[4]	Adnephrin	67.8	58.0
Cd	Adrenalin	106.0	75.0
Cm	Adrenalin	66.6	64.4
Dd	Adrin 1 : 500	0.0	0.0
Dm	Adrin 1 : 1000	0.0	0.0
Em	Caprenalin	0.0	0.0
Fd	Supracapsulin	102.6	101.6
Fm	Supracapsulin	99.0	93.4
Gd	Suprarenalin	97.6	78.6
Gm	Suprarenalin	83.0	79.0
Hd	Suprarenin synthetic	74.2	60.0
Hm	Suprarenin synthetic	73.8	60.2
Hd	Suprarenin synthetic	74.2	24.4
Hm	Suprarenin synthetic	73.8	48.0

[1] Solution made Oct. 29.

[2] Solution made Oct. 19.

[3] Series "d" bought directly from manufacturers or from their agents.

[4] Series "m" bought on the open market from a reliable druggist.

[1] *Bull.* **55**, 24–5, Hyg. Lab., U. S. Pub. Health & Marine Hosp. Serv., Wash.

[2] *Ibid.*, **61**, 25.

[3] *Bull.* **61**, 23, Hyg. Lab., U. S. Pub. Health & Marine Hosp. Serv., Wash.

Sollman and Brown[1] have also tested the relative efficiency of epinephrin solutions from different sources after allowing them to stand for a specified time. The values obtained, taking the best sample as 100, were 95, 86, 70, 63 and 0.

Gunn and Harrison[2] studied the factors which caused the deterioration of such solutions. Their results show that the container is responsible for some of the deterioration, as an acid solution of epinephrin is more stable than an alkaline solution since the latter seems to increase the rate of oxidation. They also point out that twice the minimal amount of hydrochloric acid necessary to dissolve the base will give a more stable solution. Solutions in saturated boric acid free from iron were twice as active as similar solutions in ordinary medicinal boric acid. The medicinal boric acid was not purified and it developed considerably more color than the other solution. Solutions kept in bottles only partially filled showed a rapid change in color. Dixon[3] made the physiological tests of these solutions and found that all solutions deteriorated on change of color and those solutions which had become deep red were almost inactive.

Siegel,[4] on testing the effect of oxidation upon an epinephrin solution, comes to the conclusion by using Ehrmann's reaction, the pupil dialation, that epinephrin alone or in the blood-serum is not destroyed by oxidation.

On account of the rapid deterioration of epinephrin solutions, the impure preparations and the uses of different anesthetics in the blood pressure method of assay, varying results have been obtained on the action of epinephrin. The most important diversion of opinion rests on the deterioration of an epinephrin solution and whether the epinephrin rise in the blood pressure is followed by a depression. Schultz[5] does not call attention to the action of epinephrin, but he does speak of an after-depression which invariably follows the initial effect of the drug. He does not say whether this was characteristic of his standard epinephrin, which he took every precaution to prepare (from the results obtained, it must have been perfectly pure), or whether it occurred only with the different commercial preparations.

Van Leersum[6] calls special attention to this after-depression by pointing out that it is a characteristic of epinephrin.

The disagreements in regard to the physiological action of epinephrin, both in the pure state and after-oxidation, together with the difficulty encountered in obtaining pure epinephrin from the glands of the whale, which on standardizing gave so many conflicting results, led the author to investigate other

[1] *J. Am. Med. Assn.*, **47**, 792 (1906).

[2] *Pharm. J.*, **26**, 513–4 (1908).

[3] *Ibid.*

[4] *Pflüger's*, **138**, 617–37 (1911).

[5] *Bull.* **55**, 48, Hyg. Lab., U. S. Pub. Health & Marine Hosp. Serv., Wash.

[6] *Pflüger's*, **142**, 377–95 (1911).

means for separating the epinephrin and to determine if possible the best method for its purification. It is hardly plausible that such a strong vaso-constrictor substance as epinephrin should also possess a strong depressant action.

EXPERIMENTAL.

The material for part of this investigation was obtained by the writer during the summer of the year 1910, while visiting the various whaling stations in Newfoundland and Labrador. A fresh supply of the suprarenal glands of the whale was received from the same locality, late in the year 1911. The glands were removed from the whales within twenty-four hours after death. Obtained thus under these conditions, they were fresh and were easily preserved. Chloroform was used as the preservative and on account of the size of the glands they were cut up into small pieces Five cc. of the chloroform were added to one quart of the material and the jars completely filled, so as to leave the minimum amount of air space above the glands. The majority of the glands preserved remained in good condition, which was partly accomplished by keeping them in a cool place.

The first step in the investigation was to secure the suprarenal glands from cattle, hogs and sheep and separate the active principle from these glands by Abel's and Takamine's method. The epinephrin obtained was compared with respect to its qualitative and quantitative properties and found to agree in every way. Similar tests were made on the whale epinephrin and certain peculiarities were noticed, more especially in regard to the quantitative tests. Instead of obtaining the characteristic rise of the blood pressure at once, there was a fall preceding the rise. The suprarenal glands of the whale contain large quantities of phosphates and in using Takamine's method for extracting the epinephrin from the glands, only phosphates were obtained. Abel's method also removed more phosphates from the glands than it did epinephrin. This was probably due to the old condition of the glands and not unlikely in part to the preservative. Some of the jars of whale glands were preserved and sent to me from Newfoundland. These glands contained as much as 100 cc. of chloroform to the jar. The glands from one of these jars were pressed and the solution made distinctly acid with acetic acid (50 per cent.) and boiled for about one hour on a water bath. This coagulated a part of the inert matter, which was filtered and the clear filtrate was evaporated under pressure to a small bulk The residue obtained was made alkaline with ammonia and epinephrin immediately separated out. This was repurified and gave the first good yield of epinephrin from the glands of the whale. This would indicate that epinephrin is not present in the glands as a free base, since it is not soluble in chloroform, but that it is a constituent of a more complex substance[1] which is probably broken down by the acid used in the process. Experiments are now in progress, to determine, if possible, the form of epinephrin in the glands. This led to further investigation into the methods for separating epinephrin and the following method was finally devised:

A solution containing 500 cc. absolute alcohol, 50 cc. chloroform and 25 cc. of acetic acid, was gradually added, with constant shaking, to 1000 grams of the finely disintegrated preserved glands of the whale. This was allowed to stand over night. The liquid was pressed from the glands, made distinctly acid with an additional 25 cc. of acetic acid (50 per cent.) and brought to a boil on a water bath, to coagulate the protein material. The precipitate was filtered off and 600 cc. of a clear yellowish filtrate obtained. The filtrate was concentrated under diminished pressure to 60 cc. This residue was filtered and made distinctly alkaline with strong aqueous ammonia whereupon a heavy precipitate of epinephrin formed. This was immediately collected on a filter under pressure, washed thoroughly with water, absolute alcohol and ether and dried in a vacuum over sulphuric acid. The yield on the first precipitation was 2.1103 grams.

The residual glands were treated in the same manner a second time, except that the solution contained 500 cc. of 70 per cent. methyl alcohol, 100 cc. chloroform and 25 cc. acetic acid. This second precipitation gave a yield of 0.36 gram of epinephrin.

The epinephrin was repurified by adding 20 cc. of a 25 per cent. solution of acetic acid, containing 1 cc. of sodium sulphite, to 2.0525 grams of the impure epinephrin. This dissolved the base, giving a brown solution. The solution was filtered and to the clear filtrate ammonia (sp. gr. 0.950 was added until the precipitation was complete. The epinephrin formed as a heavy white flocculent precipitate. This was allowed to stand in a cool place for about an hour. The precipitate was collected on a filter under pressure, again thoroughly washed with water, absolute alcohol, ether, and dried in a vacuum over sulphuric acid. This yielded 1.7680 grams. The second precipitation of 0.36 gram of impure epinephrin was recrystallized by the same method and gave a yield of 0.3104 gram of the pure base. This totaled 2.0784 grams of pure, almost white, crystalline epinephrin or a little better than 0.2 of 1 per cent. yield rom the moist glands. The loss in the repurification was 13.8 per cent. This method could hardly be called quantitative, yet every precaution was taken to prevent oxidation and loss through manipulation.

The same method was used for extracting epinephrin from the fresh suprarenal glands of cattle. On the first precipitation 3.2225 grams of impure epinephrin were obtained from 1000 grams of the fresh glands. This contained a large percentage of impurities, mostly phosphates. The phosphates obtained in some cases were 0.1 per cent. of the moist glands. Other impurities were also present, as will be pointed out from the physiological tests.

The whale epinephrin possesses all of the properties of epinephrin, such as giving with ferric chloride the emerald green color which quickly turns rose red on

[1] This suggestion was made by Dr. F. W. Bushong, of this laboratory. Some experimental work has been done which gives evidence of the existence of such a compound.

standing in the air, the rose-pink color with iodine, reduction of ammonical silver nitrate solution and Fehling's solution.

Nitrogen determinations by the Kjeldahl method showed the following results:

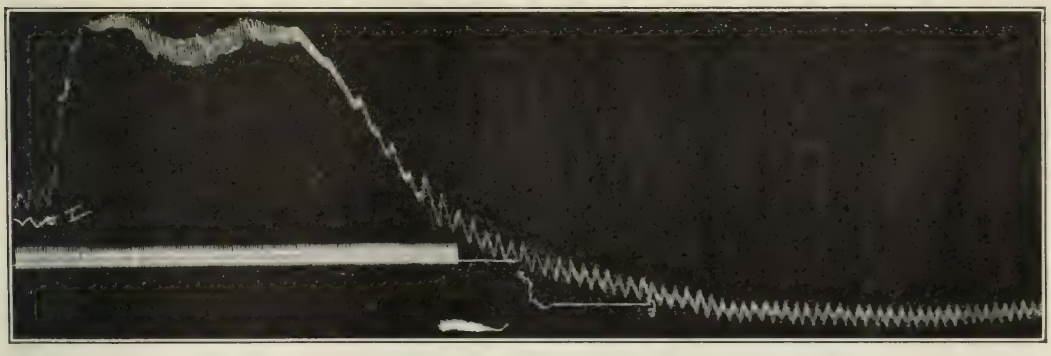
Product analyzed.	Theoretical requirements for formula $C_9H_{13}NO_3$.
N = 7.91	N = 7.65

The polarimetric reading was $[\alpha]_D^{25} = -52.00°$. The melting point was 212° C. This would indicate that the whale epinephrin is the same as the active principle separated from the glands of other mammals.

The exact yield of the epinephrin content of the whale glands is hard to determine, as the extractions were made from the glands after they had stood from six to nine months The best yield obtained was 0.2 of 1 per cent. of the moist glands and these glands were in exceptionally good condition. Most of the determinations show about 0.15 per cent. Abel[1] has described a method which is said to give a yield of 0.3 per cent. from the fresh cattle glands, and it is quite possible to expect a like yield from the fresh glands of the whale. Several tests were made to detect iodine in the glands, but all gave negative results.

As was pointed out in the early part of the paper the different commercial and synthetic preparations of epinephrin may compare very favorably in all the qualitative tests and yet the quantitative results vary widely. This was clearly demonstrated in Schultz's[2] table where only three out of seven brands of epinephrin were found to compare with the standard. The other solutions varied from 3.71 to 71 per cent of the required activity. Thus, after making sure of the qualitative properties of the whale epinephrin, every precaution was taken to obtain the best quantitative results. The success of these quantitative results was due largely to the valuable coöperation of Mr. Burket. Of the various methods investigated and tried, the blood pressure proved the most satisfactory. The method used was practically the same as that described by Schultz,[3] which indicates the change of the blood pressure in the carotid artery produced by making the injection in the femoral vein of an anesthetized animal, except that cats were used in place of dogs, and no curare was given with the ether anesthesia. The only advantage to be gained by the use of curare is to prevent muscle tremors, but this could hardly be called an advantage, since curare has a depressant action which might interfere with the action of the epinephrin. By very carefully administering the ether at specified times and between each injection, a very uniform condition of anesthesia could be maintained and the animal could just be kept in a state of unconsciousness, which condition seemed to be favorable for the best results.

The epinephrin used for these physiological tests was carefully prepared and the degree of purity was determined by testing solutions which contained impurities and solutions of the recrystallized epinephrin. Several different methods for recrystallizing the base were used. The solutions were not made up until about two hours before the experiments were performed and then they were prepared from the crystalline product. The amount of base necessary to make a 1 : 1000 solution was weighed out on an analytical balance and dissolved in Ringer's solution, containing the calculated amount of hydrochloric acid necessary to dissolve all the epinephrin. This solution was then diluted to the desired strength. The injections were usually 1 cc. of a 1–10,000 parts solution of the base. The syringe and pipettes used were standardized.



CURVE I.

Showing change in blood-pressure produced by an intravenous injection of 1 cc. of 1–10,000 parts solution of commercial epinephrin. Data under Table IV, Lab. No. I. The perpendicular lines in the curve represent the heart action and respiration; the lower line is used as a base line and to determine the time. This curve shows very clearly the characteristic after-depression obtained by the use of impure epinephrin.

The epinephrin thus prepared from the whale was compared with a commercial preparation of epinephrin obtained directly from the manufacturers and with commercial solutions of epinephrin placed upon the market.

The blood pressure experiments were made in connection with some experiments Mr. Burket was making on the influence of epinephrin modified by various salt solutions, such as sodium chloride, potassium chloride, barium chloride, salts of phosphorus and the like, on the blood pressure, in the Physiology Department of

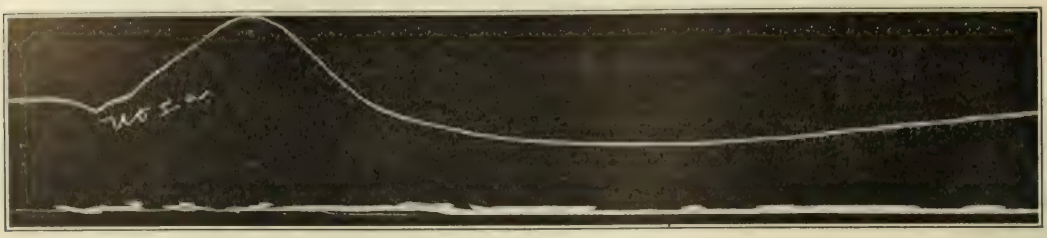
[1] *Loc. cit.*
[2] *Ibid.*
[3] *Bull.* **55**, 25, Hyg. Lab., U. S. Pub. Health & Marine Serv., Wash.

this University. The results of his research will appear in the *American Journal of Physiology*.

The blood pressure experiments were made on 17 cats, but the data from only a few of the typical experiments will be given. The greater part of this data will be confined to the active principle from the whale glands, a part that was not taken up in detail by Mr. Burket. Sufficient data will be taken from the commercial preparations to show the difference in action between the pure and impure product of both whale and cattle epinephrin, the effect of oxidation on a solution of the base and to prove the quantitative properties of whale epinephrin.

In all but one of the injections (see Table I) the epinephrin rise was followed by an after-depression which was more apparent with the commercial epinephrin than with the purer product obtained from the glands of the whale and cattle.

The method for repurifying the epinephrin used in these experiments was to dissolve the base in absolute alcohol, which contained a small percentage of dilute hydrochloric acid. The organic, inorganic and protein material was precipitated by adding ether. The solution was filtered and ammonia added to the clear filtrate until the solution smelled distinctly of ammonia, at which point the precipitation was complete. The precipitate was collected on a filter under pressure and thoroughly washed with water, absolute alcohol and ether. It was dried in a vacuum over sulphuric acid. It was found necessary to take pre-



CURVE II.

Showing change in blood pressure produced by an intraven us injection of 1 cc. of 1–50,000 parts solution of commercial epinephrin. Data under Table IV, Lab. No. Ia. The depression here is in about the same proportion to the rise as is that shown in Curve I.

TABLE I.—BLOOD PRESSURE EXPERIMENT, FEB. 21, 1912.

Male cat, 3.5 kilograms weight. Ether anesthesia. Record of the change of the blood pressure in the carotid artery. Solutions prepared 11.30 A.M. and injected into the femoral veins: 5 milligrams of the base dissolved in 5 cc. of Ringer's solution, acidulated with calculated amount of HCl and diluted to make 1–10,000 parts solution (base). Amount injected, 1 cc.

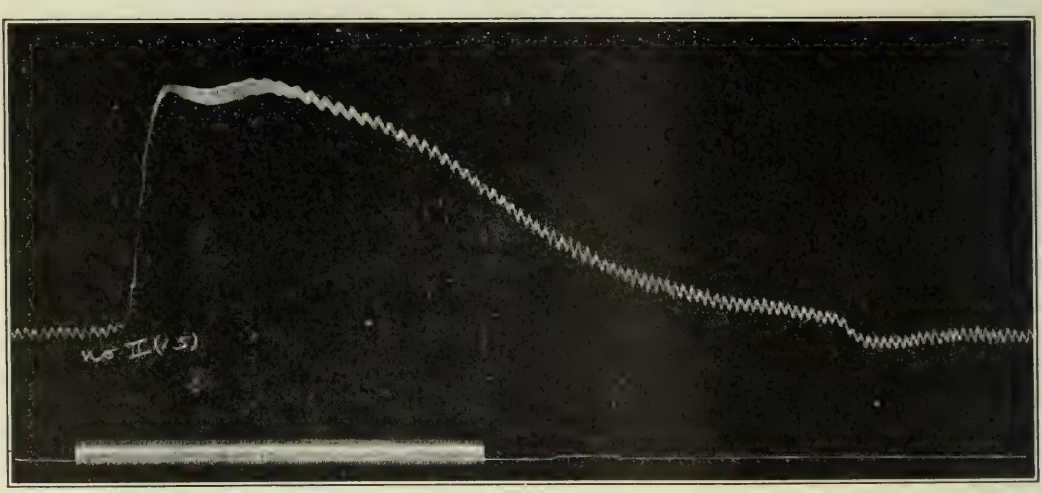
Solution injected.	Lab. No.	Time of injection.	Blood pressure measured by mercury manometer. Before.	After.	Rise.	Duration of rise.		Depression.	Duration of depression.	
		P.M.	Mm.	Mm.	Mm.	Min.	Sec.	Mm.	Min.	Sec.
Epinephrin:										
Commercial[1]	Ia	2.48	170	248	78	1	10	50	1	30
Whale "A"[2]	II	3.03	160	238	78	1	45	24	..	30
Whale "B"[3]	III	3.08	156	220	64	1	30	32	1	30
Whale "A"	IIa	3.32	160	234	74	1	..	28	..	10
Commercial	IX	3.54	120	196	76	2	..	30	1	..
Cattle[4]	X	3.57	132	212	80	2	..	none	..	..

[1] Commercial crystalline epinephrin obtained directly from the manufacturers.

[2] Recrystallized.

[3] Impure.

[4] This epinephrin was prepared by the same method used to prepare the whale epinephrin and was repurified the same as Whale "A" epinephrin.



CURVE III.

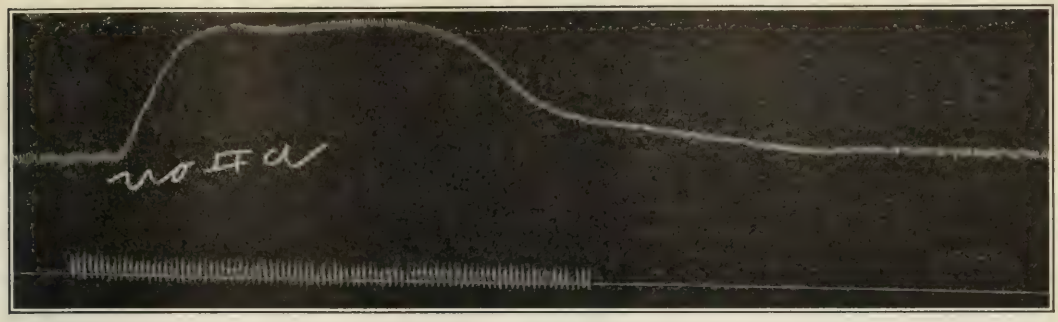
Showing change in blood pressure produced by an intravenous injection of 1 cc. of 1–10,000 parts solution of repurified whale epinephrin. Date under Table IV, Lab. No. II(15). The after-depression is entirely eliminated.

cautions in using this method, as the addition of too strong hydrochloric acid readily decomposes the base.

In Table II the after-depressions are as characteristic as the rise which appeared greater with the commercial than with the purer epinephrin.

1 cc. injection of a 1-10,000 parts solution of the base compare very favorably with those obtained by Schultz.[1]

Whale epinephrin "93" (Table III) was repurified by dissolving it in dilute acetic acid containing a small



CURVE IV.

Showing change in blood pressure produced by an intravenous injection of 1 cc. of 1-50,000 parts solution of repurified whale epinephrin. Data under Table IV, Lab. No. IIa. No depression.

TABLE II.—BLOOD PRESSURE EXPERIMENT, FEB. 24, 1912.

Male cat. Approximate weight, 3.5 kilograms. Same method and dilutions as given under Table I. Solutions were prepared by 9.40 A.M. Amount injected, 1 cc.

Solution injected. Epinephrin:	Lab. No.	Time of injection.	Blood pressure measured by mercury manometer. Before.	After.	Rise.	Duration of rise.		Depression.	Duration of depression.	
		A.M.	Mm.	Mm.	Mm.	Min.	Sec.	Mm.	Min.	Sec.
Commercial	I	10.28	160	246	86	1	7	54	2	53
Whale "A"[1]	II	10.33	156	268	112	1	30	6	1	..
Whale "A"	IIa	10.37	150	262	112	1	30	28	1	..
Whale "B"[2]	III	10.42	146	244	98	1	11	42	2	..
Commercial, 1-1000 Sol.	VI	10.54	152	218	66	..	55	22	1	40
Whale	VII	10.57	150	258	108	2	..	48	2	..
Cattle[3]	VIII	11.14	110	206	96	2	30	10	..	15
Cattle	VIIIa	11.17	116	216	100	2	..	none	.	..
Commercial	Ia	11.24	110	220	110	1	20	34	2	30
Cattle "A"[4]	X	11.43	110	198	88	2	15	none	.	..
Whale "B"	IIIa	12.05	110	198	88	1	15	42	2	..
Whale "A"	II(g)	12.24	100	208	108	2	..	8	..	10

[1] Repurified.
[2] Impure.
[3] Cattle epinephrin prepared and purified in the same manner as the whale epinephrin.
[4] Second preparation by the same method.

The same method of purification was used, as described under Table I. The increase in the blood pressure was very nearly the same for all the crystalline preparations but was a considerable increase over the commercial 1-1000 solution of the base. The results in the increase in blood pressure for a

TABLE III.—BLOOD PRESSURE EXPERIMENT, APRIL 27, 1912.

Female cat, 3 kilograms weight. Same method and dilutions as given under Table I. Solutions prepared at 9.00 A.M. Amount injected, 1 cc.

Solution injected. Epinephrin:	Lab. No.	Time of injection.	Blood pressure measured by mercury manometer. Before.	After.	Rise.	Duration of rise.		Depression.	Duration of depression.	
		A.M.	Mm.	Mm.	Mm.	Min.	Sec.	Mm.	Min.	Sec.
Commercial	Ia	10.10	130	214	84	2	..	30	1	30
Whale 93[1]	2	10.15	90	198	108	3	..	..	..	.
Whale 93	9	10.23	96	192	96	3	..	..	.	.
Whale "B"[2]	10	10.34	120	188	68	2	..	22	3	.
Whale "B"	3	10.52	100	170	70	2	..	10	1	.
Whale 892	15	11.53	90	150	60	3	..	14	2	.

[1] Repurified.
[2] Impure.

per cent. of sodium sulphite and reprecipitated by adding ammonia. This gave an almost pure white crystalline product as distinguished from the commercial preparation, which is of a pinkish color. The polarimetric measurement was $[a]_D^{25} = -52.00°$. This epinephrin failed to give the after-depression, which occurred with the injections of the commercial and impure whale epinephrin.

As can be seen by examining the table, the increase in the blood pressure lasted for a longer time with the pure epinephrin and there was no depression as characterized by the commercial and impure compound. This would indicate that the depression is due to some impurity. The following tables contain sufficient evidence to prove that the after-effect is due to some foreign substance and is not in any way a part of the epinephrin. The base used for the experiments in Table IV was repurified three times by the method

TABLE IV.—BLOOD PRESSURE EXPERIMENT, MAY 5, 1912.

Female cat. Approximate weight 3 kilograms. Method same as given under Table I. The solutions were prepared at 1.30 o'clock and diluted to make 1-10,000 (*a*) and 1-50,000 (*b*) parts solution (base). Amount injected, 1 cc.

Solution injected. Epinephrin:	Lab. No.	Dilution.	Time of injection.	Blood pressure measured by mercury manometer. Before.	After.	Rise.	Duration of rise.		Depression.	Duration of depression.	
			P.M.	Mm.	Mm.	Mm.	Min.	Sec.	Mm.	Min.	Sec.
Commercial	Ia	b	2.23	136	180	44	.	42	18	1	30
Commercial	I	a	2.27	136	228	92	2	..	34	.	30
Whale "A"[1]	IV	a	2.40	120	134	114	2	.	..	.	..
Whale "A"	II	b	2.48	120	164	44	1	..	..	.	..
Whale "A"	IIa	b	3.01	130	176	46	.	57	..	.	..
Whale "B"[2]	III	a	3.06	120	208	88	1	18	6	.	15
Whale "A"	IIa,d	b	3.22	114	166	52	1	30	..	.	..
Whale "B"	IIIa	a	3.26	116	204	88	1	56	..	.	..
Cattle "A"[3]	IVa	b	3.37	120	178	58	1	24	..	.	..
Whale "A"	IIa,f	b	3.41	120	168	48	1	15	..	.	..
Commercial	Ia,b	b	3.43	126	178	52	1	12	18	2	..
Whale "A"	IIa,g	b	3.55	112	168	56	1	30	.	.	.
Commercial	Ia,h	b	4.03	116	174	58	1	18	6	.	15
Whale "A"	II(15)	a	4 10	116	224	108	2	..	none	.	..
Commercial	Ig	a	4 15	120	212	92	2	..	18	.	30

[1] Repurified.
[2] Impure.
[3] Prepared in the same manner as the whale epinephrin.
[1] *Loc. cit.*

described under Table III in order to be absolutely certain of its purity.

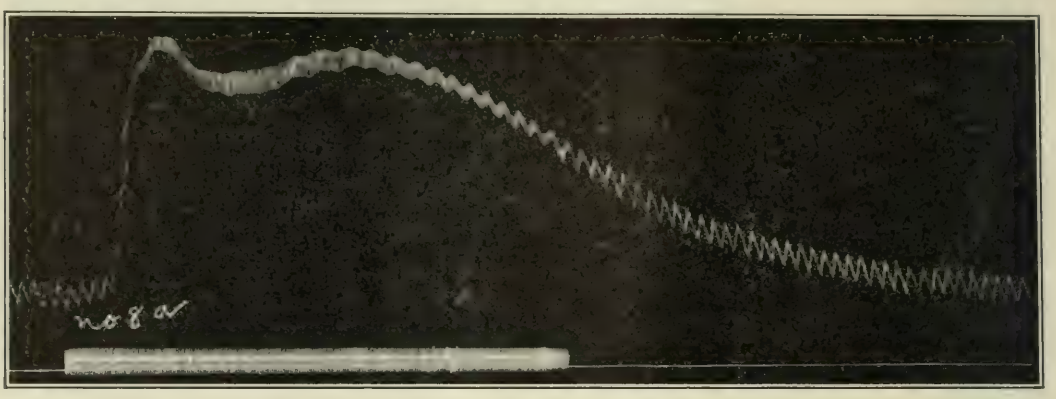
The only depressions obtained were by injecting the impure whale epinephrin and the commercial preparation. The increase in the blood pressure is just about the same with the commercial preparations as with the repurified compound. However, the effect of the drug lasted for a longer time with the pure base. These results are again in agreement with those obtained by Schultz.

It thus becomes evident that the after-effect so commonly given by epinephrin is not a characteristic of the base but is due to some other source. The difference between the pure and impure epinephrin in the increase of the blood pressure shows this depressant substance to be of a very active nature.

TABLE V.—AMOUNT INJECTED, 1 cc.

		Concentration of solution.		Blood pressure measured by a Mercury manometer.			
				Rise.	Depression.	Rise.	Depression.
Solution injected.	Lab. No.	Base. Gram.	Ringer. Cc.	Apr. 27. Mm.	(Fresh.) Mm.	May 5. Mm.	(Old.) Mm
Epinephrin							
Commercial	Ia	1	10,000	84	30	72	50
Whale "93"	2	1	10,000	108	..	86	22
Commercial Fresh, May 5	I	1	10,000	..	..	92	34
Whale Fresh, May 5	IV	1	10,000	..	..	114	none

ing failed to increase the blood pressure to the same degree as a fresh solution of the same strength of the base. The same solution injected into an anesthetized cat eight days previous possessed a stronger vasoconstrictor action than it did after standing. The



CURVE V.

Showing change in blood pressure produced by an intravenous injection of 1 cc. of 1–10,000 parts solution of repurified cattle epinephrin. Data under Table II, Lab. No. VIIIa. This curve is of the recrystallized cattle epinephrin separated by the same method as that used in obtaining the active principle from the glands of the whale and is identical with the curve produced by the whale epinephrin.

The solutions of epinephrin undergo decomposition very readily and in most cases this is clearly indicated by the color changes. A deteriorated solution will first become pink, then red and finally brown, at which point a precipitate usually is formed. It has been clearly demonstrated by many investigators that solutions having reached this stage are worthless for medicinal purposes.

A few experiments have been made to determine the effect of slightly deteriorated solutions. Only part of the solutions prepared for the physiological experiments given under Table III were used for making those tests. The remaining solutions were placed in white glass bottles, care being taken to see that the bottles were only half filled by the solutions. These were placed aside for one week. On examination, they all showed a change of color, which was more distinct with the commercial solution than with those of the purer epinephrin. The commercial epinephrin had changed to a red color, while the purer base was of a faint pink color. Physiological tests were made of these solutions, the results of which are recorded in Table V.

The injection of a solution after eight days' standincrease in the blood pressure by an injection of epinephrin varies in the different animals and this is well illustrated in experiments of Table V, in which the fresh solution of epinephrin caused a greater increase in the blood pressure than the fresh solutions injected into a different animal eight days previous; thus if the solutions Nos. I*a* and 2 in Table V had not deteriorated on standing, they should have increased the pressure more in this particular case than they did before, but as denoted by the results, the rise in the blood pressure fell considerably below the previous rise. On comparing these results with those obtained by Schultz,[1] it will be seen that they substantiate his work. As an example, he found that an injection of a 1–10,000 parts solution of "epinephrin"[2] prepared on October 29th gave an increase of 106 mm. in the blood pressure, while a similar solution prepared ten days previous increased the pressure only 75 mm. The results show that this deterioration was just the same with the pure and impure product, as in neither case was the blood pressure increase as great as with the

[1] *Loc. cit.*

[2] Schultz uses the name adrenaline instead of epinephrin in this particular case. Adrenaline is often used in the chemical literature for the active principle from the suprarenal glands.

fresh solutions It is also to be observed that the after-depression with the commercial epinephrin has increased and that the pure epinephrin, which a week previous did not give an after-effect, now produces a marked depression. It is quite possible, therefore, that part of the so-called characteristic depressant action of epinephrin is partly due to the decomposition products of epinephrin caused by oxidation, and partly due to the impurities. We may conclude, therefore, that the impurities present in an epinephrin solution perform two functions: first, their presence alone causes the epinephrin to give an after-depression, and second, they tend to accelerate the degree of the deterioration of a solution.

The impurities present in an epinephrin solution consist largely of proteins, lecithins and phosphates. In order to get a control and to see whether the phosphates, which are present in such large quantities in the glands of the whale, have any effect on the blood pressure, physiolog cal tests were made[1] on the various salts of phosphorus and on phosphoric acid alone and in solution with epinephrin. These showed no effect whatever on the blood pressure. On oxidation and decomposition, cholin, or some other substance which is antagonistic to epinephrin, might be formed in small quantities.

CONCLUSIONS.

Epinephrin is present in the suprarenal glands of the whale and can be separated from the glands preserved in chloroform after standing for six to nine months. The highest yield obtained was 0.2 per cent. of the moist glands or about 1.2 grams from each gland.

If the epinephrin is very carefully purified by the method described under Table III and injected intravenously, it gives a marked increase in the blood pressure which is not followed by a depressant action. This so-called depressant property of epinephrin is due to impurities present in the glands and to decomposition products which are formed through oxidation on standing for a short time in aqueous solution. The commercial epinephrin shows this after-depression. The commercial product used in making these comparisons was declared by Schultz to be the best preparation placed upon the market. He gave sufficient evidence to show that it increases the blood pressure to the same degree as a much purer product, and these results were duplicated in the data presented in this paper. However, as is illustrated from these results, the increase in the blood pressure alone cannot be used as an index of purity but the after-depression must also be taken into consideration.

This is illustrated by the following experiments.

Table VI contains an average change in the blood pressure produced by injecting 1 cc. of a 1–10,000 parts solution of the pure and impure epinephrin into a 3 kg. cat. This epinephrin was obtained both from the cattle and the whale.

TABLE VI.

Solution injected.	Amt. injected. Cc.	Concentration of solution. Base. Gram.	Ringer. Cc.	Blood pressure measured by a mercury manometer. Rise. Mm.	Depression. Mm.
Epinephrin:					
Commercial	1	1	10,000	84	30
Pure	1	1	10,000	108	none

[1] These were studied by Mr. Burket and the complete results will be published in his paper in the *Am. J. Phys.*

The following table contains an average change in the blood pressure produced by injecting 1 cc. of a 1–50,000 parts solution (base) into a 3 kg. cat.

TABLE VII.

Solution injected.	Amt. injected. Cc.	Concentration of solution. Base. Gram.	Ringer. Cc.	Blood pressure measured by a mercury manometer. Rise. Mm.	Depression. Mm.
Epinephrin:					
Commercial	1	1	50,000	55	8
Pure	1	1	50,000	58	0

Several different methods were used to detect iodine in the glands and they all gave negative results.

The author wishes to express his gratitude to Dr. Robert Kennedy Duncan, Sc.D., for his helpful assistance in this work.

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THE CHLORIDES OF CARBON AS SOLVENTS, I: CARBON TETRACHLORIDE.[1]

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Received June 22, 1912.

INDUSTRIAL CONSIDERATIONS.

Serious endeavors have been made to introduce carbon tetrachloride, which has replaced chloroform for many purposes, as a substitute for benzine in industrial extraction processes, and it has, in fact, been adopted in a number of industries with excellent results. For such a purpose, a solvent, to be of industrial value, should satisfy the following requirements:[2]

1. It should be free from danger of inflammability and explosion.[3] This is, as is well-known, one of the principal advantages in using carbon tetrachloride, and renders it of especial importance in the dyeing industry and in cleaning establishments.[4] When such a non-inflammable material as carbon tetrachloride is employed as a solvent, high premiums for fire insurance and special precautions against fire are reduced.

2. It should be a uniform chemical compound and not a mixture, so that only distillation, and not fractionation, should be required in practice. Carbon tetrachloride complies in full with this requirement.

3. It should be completely volatile without imparting any odor to the solute or extracted material. It has been found that bone fat produced with the aid of carbon tetrachloride is of superior quality to that

[1] Read before the New York Section of the American Chemical Society, May 10, 1912.

[2] On these points, see Ganswindt, *Z. angew. Chem.*, **1899**, 537.

[3] Carbon tetrachloride is unnflammable and furnishes no explosive vapors. On the flash points of mixtures of carbon tetrachloride and light petroleum, see Barrier, THIS JOURNAL, **2**, 16.

[4] A number of processes have been devised for rendering carbon tetrachloride soluble in dilute soap solutions and for rendering it soluble in, or emulsifiable with, water. The products are intended for use in cleansing textiles, etc. Sommerfeld (*Leipziger Färber- u. Zeugdrucker-Ztg.*, **47**, 223) pointed out that carbon tetrachloride could be used for removing grease stains, and that, unlike when petroleum spirit was used, there was no halo left after the stain had disappeared. Carbon tetrachloride has been sold as a grease eradicator for some time.

obtained by means of petroleum ether. In such extraction processes, the favorable results obtained are also to be attributed, in part, to the fact that, with carbon tetrachloride, the extraction is at a lower temperature.[1]

4. It should dissolve fats, resins, and oils as readily as benzine.[2]

5. It should not freeze at the average winter temperature. Carbon tetrachloride freezes at —24.7° C. at the ordinary pressure, and at 0° C. under 620 atmospheres pressure.

6. Its vapors, when inhaled, should not exert any objectionable physiological action. It has been stated that the use of carbon tetrachloride is objectionable from a hygienic standpoint;[3] but its anesthetic action has been investigated, and, notwithstanding many statements to the contrary, carbon tetrachloride has been found to be quantitatively less active than benzine.[4]

7. Its price should be as nearly as possible that of benzine. Comparative high cost has been the principal handicap of carbon tetrachloride.

Other worthy advantages of carbon tetrachloride than those given above, are: It has a lower boiling point—namely, 78.1° C.—than the generally employed petroleum fractions (70°–120° C.); it possesses a specific gravity of 1.63, and therefore shares with carbon disulphide the advantage of being heavier than water; and it possesses both a low specific heat (0.219 at 80° C.) and a low latent heat of evaporation, in consequence of which its use effects a great saving in steam and cooling water.

It has been indicated, however, that these advantages are not a sufficient set-off against the comparative high price of carbon tetrachloride, for, in the extraction processes by the aid of solvents, the volume of the solvent and not its weight must be considered.[5] It is evident that for the same volume of solvent more than twice as much of carbon tetrachloride by weight must be used as of petroleum naphtha.[6] The loss, expressed in actual money value, is also greater than in the case of naphtha; and it has been said that the difference in favor of carbon tetrachloride in cooling water required for condensing the vapors is too small, even though lower insurance premiums be considered, to counterbalance the difference in cost of the amounts of solvents employed. Carbon tetrachloride also attacks iron and copper, especially in the presence of moisture, so that it is necessary to use lead- or tin-lined extraction apparatus, just as in the case of *s*-tetrachloro-ethane.[1]

Pichon and Truchelut have pointed out[2] that the use of carbon tetrachloride has been restricted in many industries by its tendency to decompose, with the liberation of hydrogen chloride,[3] particularly when mixed with light petroleum. They claimed a method for suppressing this decomposition, depending upon the addition of from 1–5 per cent. of oil of turpentine or other hydrocarbon with a great affinity for oxygen.

Baskerville and Hamor[4] find that while pure carbon tetrachloride is subject to oxidation, carbonyl chloride being formed, when exposed to light in partially filled colorless glass containers for long periods,[5] and that this decomposition is accelerated by the presence of hydrochloric or sulphuric acid, yet the oxidation is much slower than in the case of chloroform. The small amount of sulphur or carbon disulphide, or both, present in commercial carbon tetrachloride may act as a preservative, and there has been very little complaint among consumers about the decomposition of the solvent. Carbon tetrachloride should not, of course, be used in the presence of oxidizing agents or mineral acids; and when it is to be kept for some time, should be stored in a dark, cool place, in well filled, or, better still, totally filled containers.

Notwithstanding the objections which have been urged against the employment of carbon tetrachloride, it has admittedly taken a place as an industrial solvent; its high solvent power for various substances, its uniformity, non-inflammability and non-explosibility, have particularly impressed certain manufacturers, and it has replaced benzine and carbon disulphide in some plants where risks from fire or explosion are serious considerations. With suitable extraction apparatus, the losses during extraction processes should be small and the solvent should do its work rapidly and economically.

[1] On this point see Brücke, *Chem. Rev. Fett- u. Harz-ind.*, **12**, 100.

[2] Von Schwartz ("Fire and Explosion Risks," p. 256, 1904) refers to carbon tetrachloride as "the best of all substitutes for benzine" and states that it "dissolves fat as readily as benzine."

[3] Von Schwartz, *ibid.*

[4] Lehman, *Chem.-Ztg.*, **1906**, 330; cf., however, Goehrig, *J. Soc. Chem. Ind.*, **22**, 1344.

On the physiological action of carbon tetrachloride, see also B. and F. *Med.-Chir. Rev.*, **1867**, 551; *Lancet*, June, 1867; Richardson, *Sci. Am. Suppl.*, No. 515, 8227; Bianchini, *Stazione Sperimentale Agraria Italiana*, **37**, 171 (1904); Freyss, *Chem.-Ztg.*, **1903**, 1137; Haller, *Ber. ueber die Weltausstellung in Paris*, **1900**; Morel, *Compt. rend.*, **84**, 1460; and Regnauld, *Idem.*, **100**, 1146.

While it is stated that carbon tetrachloride is more toxic and more irritating to the mucous membrane of the trachea and bronchi than chloroform (Francis and Fortescue-Brickdale, "The Chemical Basis of Pharmacology," **1908**, p. 97), Cushny states that its heart depressing action is one-half as strong as that of chloroform, and Marshall found the difference in action between carbon tetrachloride and chloroform to be mainly due to physical characteristics.

Carbon tetrachloride has been used by hairdressers to clean the hair, and a case of accidental poisoning, owing to the inhalation of the vapor, has been reported (*Lancet*, **1907**, i, 1725). This case very nearly had a fatal termination.

[5] See Zänker, *Leipziger Färber- u. Zeugdrucker-Ztg.*, **48**, 237.

[6] In washing operations, generally speaking, equal volumes have to be taken for comparison.

[1] Bolis (*Chem.-Ztg.*, **30**, 1117) found that perfectly dry carbon tetrachloride might be boiled in cast-iron vessels and would exert very slight action on them; but that if moisture was present, the iron was very sensibly attacked, the rate of attack increasing with the proportion of moisture. Brücke (*loc. cit.*) reported that ordinary iron extraction apparatus was quite unsuitable for carbon tetrachloride.

[2] French Patent, 402,235, April 20, 1909.

[3] Carbonyl chloride is produced by the action of powerful oxidizing agents, such as, for example, chromic acid, on carbon tetrachloride (Schmidt, *Pharm. Chem.*, **2**, 148 (1896)). Goldschmidt reported (*Wien. Akad. Ber.*, 2, *Abt.* **83**, 736; *Ber.*, **14**, 927) that water and carbon tetrachloride form hydrogen chloride and carbon dioxide at high temperatures.

For a résumé of the deportment of carbon tetrachloride with various inorganic and organic compounds, see Margosches, *Der Tetrachlorkohlenstoff*, **1905**, 45–72; and on the pyrogenic reactions of the compound, consult Regnault, *Ann.*, **33**, 310; *Ann. chim. phys.*, [2] **71**, 353; Kolbe, *Ann.*, **54**, 147; Basset, *Chem. News*, **20**, 175; Lüdeking, *Phil. Mag.*, [5] **33**, 521; Hodgkinson and Lowndes, *Chem. News*, **58**, 187; Löb, *Z. Elektrochem.*, **7**, 903.

[4] Unpublished investigation.

[5] The exposures were made for one year, to diffused sunlight and at 20° C., in bottles containing varying amounts of air.

In this connection, see Baskerville and Hamor, THIS JOURNAL, **4**, No. 4, 287.

THE SOLVENT PROPERTIES OF CARBON TETRACHLORIDE.

With regard to the solvent properties of carbon tetrachloride, very few data are available with reference to pure chemical substances. For the most part, medicinal preparations have alone been studied, and these are all very sparingly soluble.[1] Inorganic salts have received little consideration; and while such substances as acetic acid, bromine, iodine, and carbon dioxide have been investigated as to their distribution in the system water-carbon tetrachloride, yet the results give no indication of the actual solubility of these in carbon tetrachloride.

The solution of gums, resins, natural pitches, asphalts, etc., in carbon tetrachloride has been reported,[2] but the results have received only partial confirmation, —in fact, many of the statements relating thereto are conflicting. Gum mastic, for example, has been reported to be both soluble and insoluble in hot carbon tetrachloride, while, as a matter of fact, it is completely soluble at +20° C. Andes[3] reported on gums, resins, etc., insoluble, partly soluble, and soluble, which might be more easily dissolved by admixture of other solvents, as alcohol, turpentine, and the like, for producing varnishes.

Carbon tetrachloride has been used for extracting fats,[4] oils,[5] waxes,[6] asphalt,[7] resins,[8] dyes,[9] alkaloids,[10] and for dissolving caoutchouc;[11] but in the published accounts of these applications no mention of quantitative data is made.

This investigation was undertaken with the following ideas in mind:

1. To learn if the chlorides of carbon would answer the purposes of some of the solvents used at present on a large scale commercially or as analytical reagents.

2. To determine, provided they proved commercially desirable, if they supplied a less hazard to life in their use.

3. To learn if some means might be devised whereby these solvents, some already proven of value in specific cases, both as to hygiene and efficiency, could be produced at a less or at least more reasonable price.

This communication presents some new data on carbon tetrachloride as a commercial solvent. Other phases of the topic will be presented in later papers.

EXPERIMENTAL.

In the experimental determinations of the solvent properties of carbon tetrachloride, commercial carbon tetrachloride, 99.70 per cent. pure, was used.[1] All determinations were made at room temperature, which varied from 20°–21° C.—an amply close range for the work. The solvent with an excess of the solute[2] was placed in a glass-stoppered flask of suitable size and occasionally agitated at room temperature until a saturated solution was obtained; the solution was then filtered as rapidly as possible into a covered tarred dish, and weighed; and finally it was evaporated at 60° C. and the residue weighed. Viscous solutions were filtered by forcing them through absorbent cotton by the aid of compressed air. In the case of volatile solids such as camphor, it was found that these could be examined most easily by weighing an amount of solvent in a small ground-glass-stoppered weighing flask and then adding small quantities of solute until saturation was reached; the weight of the solution obtained in this manner gave the weight of actual solute. The results obtained by the authors during the course of an investigation of the solvent action of carbon tetrachloride on various substances are given below.

ASPHALTS, BITUMENS, ETC.—This class of natural and artificial products includes many which differ from each other in a variety of reactions, based mainly, however, on their solubility or insolubility in various solvents. Carbon tetrachloride has been employed in connection therewith principally for analytical purposes.

Richardson and Forrest[3] have called attention to the use of carbon tetrachloride as a solvent for differentiating between bitumens. Some of these are soluble in carbon disulphide and insoluble in carbon tetrachloride, and the quantities of such "carbenes"[4] present give an indication of the weathering or excessive heating, or both, to which a natural asphalt has been subjected.

Gilsonite is almost completely soluble in carbon tetrachloride. It is the purest natural bitumen

[1] See appended Tables.

[2] In, for example, *Neueste Erfind. u. Erfahrungen*, **1896**, 3.

[3] *Chem. Rev. Fett- u. Harz-Ind.*, **12**, 157 (1905).

[4] On the determination of fat in food materials, see Bryant, *J. Am. Chem. Soc.*, **1904**, 568. Mention has already been made of carbon tetrachloride as a fat solvent.

[5] *E. g.*, in the determination of oil in cottonseed products (Herty, Smith, and Orr, THIS JOURNAL, **1**, No. 2).

[6] In the analysis of paraffin, Graefe, *Chem. Rev. Fett- u. Harz-Ind.*, **1906**, 30. In German Patent, 179,449, January 3, 1902, fat or wax is extracted from moist substances by using, among other solvents, carbon tetrachloride; and in English Patent, 741, January 13, 1908, to moderate the chlorination reaction on resins, gums, wax, fats, oils, etc., these are dissolved in carbon tetrachloride.

[7] See Richardson and Forrest, *J. Soc. Chem. Ind.*, **24**, 310.

[8] On carbon tetrachloride as a paint or varnish diluent, see Le Roy, *Rev. Chim. Ind.*, **11**, 173. Le Roy gave the advantages as follows: diminished inflammability, less tendency for the pigment to deposit on keeping, freedom from solidification or resinification during storage, brilliant strong films, and excellent drying power.

In U. S. Patent, 817,141, April 3, 1906, to Ellis, carbon tetrachloride in combination with wax, alcohol, and amyl acetate is claimed as a paint and varnish remover.

[9] In the determination of dyes in confectionery, Pintte and Bentivoglio, *Gazz. chim. ital.*, **1906**, ii, 385. On the solution of fatty color lakes in carbon tetrachloride, see Sommerfeld, *loc. cit.*

[10] See Schindelmeiser, *Chem.-Ztg.*, **1901**, 129.

[11] In the preparation of an antiseptic rubber solution for clinical use, Wederhake, *Med. Klin.*, **1908**, 1302.

[1] The carbon tetrachloride used in this investigation was generously supplied by The Dow Chemical Company, of Midland, Mich.

[2] All of the samples of commercial products used in the work were obtained from reliable concerns. The authors are grateful for the assistance which was rendered by a number of houses in securing correct samples with their true designations, and are particularly appreciative of the following presentations:

Graded varieties of Arabic, Senegal, Indian and Tragacanth gums from Thurston and Braidich.

Animal and vegetable oils from Mr. Henry A. Gardner.

A very fine collection of commercial shellacs, also some natural and artificial bitumens from John R. Anderson and Company.

Vegetable and mineral waxes from Mr. D. Steengrafe.

All grades of commercial rosin from A to WW from George L. Hammond and Company.

Cellulose nitrate and cellulose acetate from The Arlington Company.

The other samples used were purchased in the open market.

[3] *Loc. cit.*

[4] Richardson, "The Modern Asphalt Pavement," 1st Ed., p. 120.

(99.5 per cent. pure) and absorbs carbon tetrachloride, being miscible in all proportions.

Grahamite, while an almost pure bitumen, is, unlike gilsonite, almost entirely insoluble in 62° naphtha and is 55–80.6 per cent. insoluble in carbon tetrachloride.[1]

Albertite is partly soluble in carbon tetrachloride.

Oil asphalt and *Refined bitumens* are from 99.0–99.9 per cent. soluble in carbon tetrachloride.

Andes[2] states that *Syrian asphalt* and probably all others are soluble in carbon tetrachloride.

Other solid bitumens and their deportment with carbon tetrachloride are: *Wurtzilite* (elaterite, tabbyite, aeonite, aegerite), slightly soluble; *Wiedgerite* ("mineral liver"), soluble; and *Impsonite*, partly soluble.[3] Ozokerite is considered among the waxes.

CELLULOSE, ACETATES AND NITRATES.—Like chloroform carbon tetrachloride is a *Pyroxylin* nonsolvent; it dissolves *camphor*, but, unlike chloroform, does not dissolve the *cellulose acetates*. The results of the determinations of the authors show that the *cellulose nitrates* (11.32 and 12.63 per cent. nitrogen) and *cellulose acetates* (three varieties), as well as *Celluloid*, are insoluble in carbon tetrachloride at 20° C.

It may be noted here that the authors found that 100 g. of carbon tetrachloride would dissolve 125 g. of *camphor* at 20° C.

RUBBER.—While carbon tetrachloride is a recognized solvent for rubber, no figures on its solubility can be determined with our present knowledge and methods. Like oils, waxes and fats, rubber will absorb or dissolve considerable quantities of carbon tetrachloride without assuming a liquid state. Furthermore, the amount of solvent necessary to produce a solution of definite viscosity varies with the same grade of rubber; for example, a rubber which has been masticated very much will form a more liquid solution than one which has not been worked in this way. The many grades of rubber which come into the markets all deport more or less differently, aside from the variations in each grade due to mechanical treatment; and besides, the moisture content of two samples masticated to the same extent, but dried differently, will also affect the character of the solution.

In the experiments conducted by the authors, the following grades of rubber were tried: *Up-river pure para*, *guayule*, *pale Ceylon crep*, *dark Ceylon crep*, *equateur*, and *pontianac*. It was found that 25 g. of the better grades (all except guayule and pontianac) would easily dissolve 200 g. of carbon tetrachloride, and much more carbon tetrachloride was necessary to obtain a flowing solution. It may be noted here that, according to Woudstra,[4] caoutchouc is a true colloid and the viscosity of its solutions decreases with standing.

The use of carbon tetrachloride in the purification of caoutchouc has been claimed in French Patent 404,307, June 22, 1909, of the General Caoutchouc Co., Ltd.[5]

[1] Richardson, *Ibid.*

[2] *Loc. cit.*

[3] See "Mineral Resources of the United States," **1910**, ii, 836.

[4] *Z. Chem. Ind. Kolloide*, **5**, 31 (1909).

[5] The process is for the purification of a caoutchouc by rendering it viscous with carbon disulphide or carbon tetrachloride, then treating with a solvent which will extract resin, but which will not dissolve caoutchouc.

ALCOHOL GUMS.—Of the gums of this class, mastic, sandarac, and sed accroides were tried. *Accroides* showed no solubility in carbon tetrachloride.

Sandarac was found by Coffignier[1] to be 77–79 per cent. insoluble in carbon tetrachloride, while Andes[2] reported that it was insoluble, but, like yellow accroides and mastic, dissolved on adding small amounts of alcohol or turpentine. The authors found that sandarac is partly soluble in carbon tetrachloride, although no attempt was made to ascertain the proportion. Boiling a small amount of sandarac with a large excess of carbon tetrachloride did not effect complete solution; but the soluble portion yielded, on evaporation, a light yellow resinous mass, clear and brittle.

Notwithstanding the findings of Andes, experiments showed that mastic dissolves completely in carbon tetrachloride at 20° C., forming a light yellow, very viscous solution. However, a true solubility can hardly be spoken of, owing to mutual solubility. Filtration was effected through cotton with compressed air; and on evaporating the viscous solution at 60° C., no constant weight was obtained even after 300 hours: decomposition had set in, although mastic alone is unaffected under the same conditions.

COPAL GUMS.—Margosches[3] has stated that melted Zanzibar Copal, and probably all other melted copals, are soluble in carbon tetrachloride. Andes[4] reported that hard Manila copal is insoluble, swells in the solvent when in a fine powder, but is completely soluble upon the addition of a small amount of alcohol or turpentine.

The authors find that the natural copals act differently according to their origin, but that they are all partly soluble at 20° C.; heating does not assist solution, the gums partly melting and decomposing even before all the carbon tetrachloride is expelled. In the experiments made, the ground copals were agitated with carbon tetrachloride.

Zanzibar copal is slightly soluble in carbon tetrachloride and the insoluble portion has a very slight tendency to gum together (swelling).

The *Manila copals* exhibit this gumming or swelling to a marked degree, all the fine particles adhering and forming a soft film on the solution, which film may be pulled, although it possesses no elasticity; *i. e.*, it does not return to its original shape as happens with rubber.

The *Congo copals* deport similarly to Manila copal, while *Pontianac copal* has much similarity to Zanzibar copal.

Sierra Leona copal swells up and gums much more than the above mentioned, and is partly soluble.

Brazilian copal is partly soluble without gumming, while *Brazil gum copal* in small fragments swells in the solvent.

DAMAR GUM.—This gum is completely soluble in carbon tetrachloride, giving a turbid solution which clears up on adding 95 per cent. alcohol or on warming.

[1] *Bull. soc. chim.*, **27**, 549 (1902).

[2] *Loc. cit.*

[3] "Der Tetrachlorkohlenstoff," Vol. 10, *Sammlung Chem. u. Chem-tech. Vortraege*, **1905**, p. 99.

[4] *Loc. cit.*

The solution filters easily. On evaporating the solvent at 60° C., some decomposition seems to occur, as shown by a darkening of the gum. Evaporation to constant weight showed that 100 g. of carbon tetrachloride dissolve 7.13 g. Batavia damar at 20° C.

KAURI GUM.—Several samples, ranging in quality from the finest to the most ordinary Kauri gum, were powdered and then treated with carbon tetrachloride. After standing, with occasional agitation, for several days, it was found that the gum was attacked to a certain extent, although not uniformly. Coffignier[1] has made an extensive study of Kauri gum. He found that brown hard Kauri gum gave a yellow solution and dark brown residue; that bush Kauri gum swelled and left a dark brown residue; and that bush-gathered gum afforded a pale yellow carbon tetrachloride solution and a dark brown residue. His results are, while interesting, of doubtful value; for the raw material is of variable character, probably between wide limits, and the components have yet to receive careful study. Some of these components deport differently from others, and although two samples of gum may have the same trade grading, yet their chemical and physical reactions may differ widely.

WATER GUMS.—Samples of different grades of *aleppo, Turkey* and *Persian gum tragacanth, Indian gum, gum senegal,* and *gum arabic* were treated with carbon tetrachloride. After standing for several days, with agitation, 50–70 g. of the solution were filtered and evaporated. The residue in all cases amounted to but a trace; consequently, this class of gum shows practically no solubility in carbon tetrachloride. After treatment with carbon tetrachloride, the gums did not exhibit any apparent physical change.

SHELLAC.—Andes[1] reported that shellac is insoluble in carbon tetrachloride, but that it is soluble in a mixture of 70 g. carbon tetrachloride and 30 g. 25 per cent. alcohol. Experiments by the authors on four samples—*Superfine Quality, TN Quality Native Shellac, A. C. Garnet Shellac,* and *Refuse Lac*—confirm the work of Andes.

The authors found that the *superfine* gave a negligible extract residue; that the *TN native* gave 0.2 per cent. residue from the solution, this residue being slightly turbid and brittle; that the *A. C. garnet* gave 0.2 per cent. residue, this consisting of a transparent non-brittle wax-like substance; and that *refuse lac* gave 0.2 per cent. residue also, this being very similar to shellac wax.

ROSIN.—Rosin of four different commercial grades was treated with carbon tetrachloride, and apparently a true solution resulted. This solution was difficult to handle, being exceedingly viscous; to remove undissolved rosin and grit, the solution was forced with compressed air through absorbent cotton into a tared dish. Evaporation, made at 60° C., was very slow.

Even after heating for over 350 hours at 60° C., the filtered solutions did not attain a constant weight; a blank showed only very slight losses under the same conditions. Other experiments seemed to show that not only does rosin dissolve in carbon tetrachloride, but that carbon tetrachloride also dissolves in rosin; furthermore, that a small amount of carbon tetrachloride with rosin gives a solid solution. Under such conditions, it is, of course, impossible to supply exact data as to the actual amount of rosin soluble in carbon tetrachloride.

The experimental results of the authors seem to indicate that the depth of color of a carbon tetrachloride solution of rosin may be employed to fix the grade of the sample.

PINE OIL.—Crude pine oil was found to mix in all proportions with carbon tetrachloride with, however, the formation of a white precipitate. Very small amounts of carbon tetrachloride were found to give no visible precipitate, and it was found that the production of a turbidity or white precipitate was due to the presence of water in the pine oil.

Fractional distillation products, refined and decolorized, were also available; these were: 156°–165°, 165°–177°, and 177°–195° C. None showed any precipitate with carbon tetrachloride and all mixed perfectly in all proportions.

WAXES.—The following waxes were treated with carbon tetrachloride: flora carnauba wax and No. 3 ceara carnauba wax, Japan wax, pure ozokerite, candellila wax, montan wax, yellow Cuban beeswax, bayberry wax, shellac wax (m. p. 75° C.), paraffin wax refined (m. p. 120° C.).

All of these absorb carbon tetrachloride at 20° C.; and, according to the amount of this solvent used, the resulting mass will be more or less solid or semi-fluid.

Ozokerite shows this most plainly, forming a homogeneous product in all proportions with carbon tetrachloride.

The *carnauba waxes* appear to be a distinct mixture of substances of different properties. The addition of a small amount of carbon tetrachloride softens the whole mass and further additions will finally give two layers on standing, the upper layer carrying the insoluble portion of the wax as a bulky flocculent mass, while the lower is very fluid.

Beeswax acts like carnauba wax, except that a liquid portion can be separated from the semi-solid residue without having it all suspended in the solution. It is interesting to note that the liquid portion carries the coloring matter, while the residuum is nearly white. Upon melting the latter on water, a product is obtained which hardly differs from the original wax, except that the color is gone, also some of the characteristic odor, and the product may be slightly harder.

Japan wax absorbs carbon tetrachloride more readily than the others above mentioned, forming at first a turbid semi-fluid mass. Upon the addition of more carbon tetrachloride, the fluidity increases, and finally a perfectly clear solution is obtained, although this point can not be sharply defined since the colorless particles in suspension which form the turbidity cannot be seen when the point of complete solution is approached. A portion of the turbid solution was

[1] *Loc. cit.*

filtered and evaporated, and the solubility figures 31.9 g. in 100 g. of carbon tetrachloride at 20° C. were obtained.

Montan wax acts similarly to carnauba wax, and the suspended wax is so sticky that it will totally obstruct any filter almost immediately. The addition of more solvent to permit of filtration would introduce the question as to whether the solution would then be saturated, and no practical method of determining this is known to the authors. The addition of a large excess of solvent leaves two layers on standing—a turbid solution below and the insoluble portion of the wax.

TABLE I.—THE SOLUBILITY OF VARIOUS INORGANIC SUBSTANCES IN CARBON TETRACHLORIDE.

Substance	Solubility in 100 g solvent.	Temperature.	Authority.
Chlorine[1]	10.5	0°	Dow Chemical Co.
Chlorine	7.4	15°	Dow Chemical Co.
Chlorine	5.56	25°	Dow Chemical Co.
Chlorine	3.02	40°	Dow Chemical Co.
Chlorine	1.17	55°	Dow Chemical Co.
Chlorine	0.81	65°	Dow Chemical Co.
Iodine	3.033	25°	Jakowkin, *Z. phys. Chem.*, **18,** 590 (1895).
Sulphur	0.717	20°	The authors.
Mercuric chloride	0.002	18°–20°	Sulc, *Z. anorg. Chem.*, **25,** 401.
Mercuric iodide	0.006	18°–20°	Sulc, *Ibid.*
	0.094	75°, b. p.	
Mercuric cyanide	0.001	18°–20°	Sulc, *Ibid.*
Stannic iodide	100 g. sol. (density 1.59) at 22.4° contain 5.25 g.		McDermott, *J. Am. Chem. Soc.*, **33,** 1963 (1911).
Stannic iodide	100 g. sol. (density 1.63) at 50° contain 8.21 g.		McDermott, *Ibid.*

[1] The use of a solution of chlorine in carbon tetrachloride in analytical chemistry is being investigated in this laboratory by Dr. L. J. Curtman.

It would seem that montan wax is undoubtedly a mixture of several components which differ materially from each other in their properties.

Candelilla wax.—What has just been said of montan wax applies equally well to candelilla wax.

All the above-mentioned waxes dissolve completely and easily in carbon tetrachloride at or near its boiling point, although the solutions may show a slight turbidity depending upon the amount of solvent present. A very small amount of carbon tetrachloride introduced into the melted wax dissolves completely. Accordingly, it may be said that waxes are partially

TABLE II.—THE SOLUBILITY OF NAPHTHALENE IN CARBON TETRACHLORIDE.

Solubility in 100 g. solvent.	Temperature.	Authority.
9.0	0°	Schroeder, *Z. phys. Chem.*, **11,** 457 (1893).
14.0	10°	Schroeder, *Ibid.*
20.0	20°	" "
23.0	25°	" "
26.5	30°	" "
35.5	40°	" "
47.5	50°	" "
62.5	60°	" "
80.8	70°	" "

soluble in cold carbon tetrachloride, completely soluble at or near the boiling point, and that the melted wax mixes in all proportions with carbon tetrachloride.

Fats, Tallow, etc.—The rendered animal fats, tallow, etc., are soluble in all proportions in carbon tetrachloride, and on melting yield clear solutions. According to the proportion of fat to solvent, the mixture may be from an opaque solid to a clear liquid in the cold (*i. e.*, at 20° C.).

Butter is heterogeneous and only partially soluble, the fatty components being taken up by the carbon tetrachloride. In the presence of water, on heating, an emulsion is formed which, on standing, separates into three layers, namely, the water-extract above, the carbon tetrachloride below, and very likely the casein between, since casein is insoluble in either.

Fatty Oils.—The solubility of the following oils was determined: menhaden, whale, linseed (raw and boiled), corn, untreated Chinese wood, soya, and cottonseed. It was found that all of these are miscible in all proportions with carbon tetrachloride.

TABLE III.—THE SOLUBILITY OF CARBON TETRACHLORIDE IN WATER.

Solubility in 100 g. water.	Temperature.	Authority.
0.097	0°	Rex, *Z. phys. Chem.*, **55,** 355 (1906).
0.083	10°	" *Ibid.*
0.080	20°	" "
0.085	30°	" "

In order to determine the value of carbon tetrachloride as an extracting solvent, 10 g. of each oil, with the exception of cottonseed, were mixed with 25 cc. of carbon tetrachloride and then evaporated at 60° C., a blank with 10 g. of each oil being heated at the same temperature for the same length of time. The period of heating varied from $5^1/_4$ hours to 10 hours, depending upon the rapidity with which the solvent evaporated. The following results were obtained:

Menhaden oil, after six hours heating, gained less

TABLE IV.—THE SOLUBILITY OF VARIOUS MEDICINAL PREPARATIONS IN CARBON TETRACHLORIDE.

Substance.	Solubility in 100 g. solvent.	Temperature.	Authority.
Aconitine (amorphous)	1.99	18°–22°	Mueller, *Apoth.-Ztg.*, **18,** 2 (1907).
Brucine	0.078		Mueller, *Ibid.*, 232.
Brucine	1.937	17°	Schindelmeiser, *Loc. cit.*
Atropine	1.136	17°	Schindelmeiser, *Loc. cit.*
Caffein	0.089	18°	Goeckel, *J. Chem. Soc.*, **74,** 327 (1898).
Caffein	0.702	Boiling	
Chinine, hydrate	0.203		Mueller, *Loc. cit.*
Chinine, anhydrous	0.529		Prunier, *J. Pharm. Chim.*, [4] **29,** 136
Chinidine	0.565		
Cinchonin	0.0361		
Cinchonidin	0.0508		
Cocaine	18.503		Schindelmeiser, *Loc. cit.*
Codein	1.328		Schindelmeiser, *Loc. cit.*
Hydrastine	0.123		Mueller, *Apoth.-Ztg.*, **18,** 249.
Hyoscyamine	0.059		Mueller, *Ibid.*
Morphine	0.0156	18°–22°	Mueller, *Idem.*, 257.
	0.032	17°	Schindelmeiser, *Loc. cit.*
Narcein	0.011	17°	Schindelmeiser, *Loc. cit.*
Papaverine	0.203	17°	Schindelmeiser, *Loc. cit.*
Strychnine	0.158	20°	Mueller, *Loc. cit.*
	0.645	17°	Schindelmeiser, *Loc. cit.*
Theobromine	0.0212		Goeckel, *Chem. Centr.*, **1897,** ii, 401.

than 1 per cent. The appearance of the oil was not noticeably altered, although the odor appeared to be stronger than in the original sample.

Linseed oil, boiled, gained 1.25 per cent. after 5 hours and 40 minutes.

Linseed oil, raw, gained 1 per cent. after 5 hours and 20 minutes.

These oils skinned slightly during the period of heating, and it is probable that the solvent may be removed only under reduced pressure and at a low temperature so as to leave the oil unchanged.

Chinese wood oil.—In 5 hours and 15 minutes the sample to which carbon tetrachloride has been added

skinned over to a considerable extent and gained 2.30 per cent. The blank showed only light skinning and an increase of but 0.27 per cent.

Whale oil gained 0.6 per cent. in 6 hours. The appearance and odor were not changed

Corn oil.—Eight hours heating was necessary in order to obtain a constant weight; a very small loss (0.04 per cent.) resulted, due possibly to the presence of water in the sample. There was no apparent change in either odor or appearance.

Soya oil.—After 7 hours the sample to which carbon tetrachloride had been added showed an increase of 0.5 per cent., while there was no gain in the blank. After heating for $3^1/_2$ hours longer, the mixed sample had gained 1 per cent. and the blank 0.3 per cent. It therefore appears that Soya oil will stand heating for some time before giving any indications of oxidation. Heating somewhat intensified the odor.

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ON THE SURFACE TENSION OF SILICATE AND BOROSILICATE GLASSES.

By EDWIN WARD TILLOTSON, JR.

Received July 1, 1912.

In a former paper[1] from this laboratory, a simple and convenient method was described for measuring the surface tension of molten glasses. This method consisted, briefly, in the determination of the relation between the weight of the drops falling from glass fibers of known diameter, which were lowered vertically into the carefully regulated flame of a blast lamp. It was found that the weight of the drop was within limits a parabolic function of the diameter of the fiber and to be expressed by the following equation:

$$W = \alpha D + \beta D^2$$

when W is the weight of the drop, D the diameter of the fiber, α a factor proportional to the surface tension and, β a factor dependent on the cohesion of the molten glass. This factor β seemed to be nearly constant for a considerable number of borate glasses, although it varied widely for some of the silicates.

The present paper is a record of surface tension determinations made on some sodium silicates, soda lime and soda-barium glasses, and also soda barium glasses containing boric oxide. For these measurements about ten fibers were drawn from each glass, varying roughly from 0.10–1.00 mm. in diameter, the drops formed in the manner previously described, and weighed. In every glass examined the parabolic relation of the diameter of fiber to weight of drop was observed and it was found that this was satisfied by a value of 15 for β in all of the glasses. This value for β is not an exact one, nor can it be accurately calculated from so few measurements. There are many causes which contribute to variations in the weight of individual drops. Inhomogeneity of the glass, errors in measurement of the diameter of the fiber, momentary changes in the condition of the flame—all may effect the weight of the drop. It is therefore necessary to make many measurements on the same glass in order to fix the exact value of β. But since for these glasses a difference of one unit in β produces a variation in the surface tension of only 2 dynes and since this is small in comparison to that introduced by variations of individual drops, the value 15 was adopted for β in all of these glasses That this procedure was justified is shown by the fact that the values for α were neither progressively higher nor lower as the diameter of the fibers increased.

[1] Tillotson, THIS JOURNAL, **3**, 631 (1911).

TABLE I.—SODIUM SILICATE GLASSES.

SiO_2. Per cent.	Na_2O Per cent.	T = dynes per cm. Obs.	Calc.
49.3	50.7	142	145
59.2	40.8	142	142
66.4	33.6	136	139
73.1	26.9	133	137
74.5	25.5	138	137
77.5	22.5	138	137
77.3	22.7	137	136

TABLE II.—SODA BARIUM GLASSES.

SiO_2. Per cent.	BaO. Per cent.	Na_2O. Per cent.	T = dynes per cm. Obs.	Calc.
70.10	6.50	23.40	144	140
66.15	13.00	20.85	145	144
61.70	19.80	18.50	150	148
57.30	26.57	16.13	164	151
53.00	33.60	13.40	153	155
48.37	40.70	10.88	155	159
71.70	5.65	22.65	138	140
67.60	12.55	19.85	143	143
64.55	18.45	17.00	151	146
61.36	24.17	14.47	150	149
58.30	29.70	12.00	148	152

TABLE III.—SODA LIME GLASSES.

SiO_2. Per cent.	CaO. Per cent.	Na_2O. Per cent.	T = dynes per cm. Obs.	Calc.
73.60	2.50	23.90	137	141
72.32	5.18	22.50	152	146
70.85	8.25	20.90	146	151
69.30	11.70	19.00	158	158
67.40	15.60	17.00	166	165
65.20	20.20	14.60	172	173

TABLE IV.

SiO_2. Per cent.	B_2O_3. Per cent.	BaO Per cent.	Na_2O Per cent	T = dynes per cm. Obs.	Calc.
63.94	3.88	15.78	16.40	145	142
52.76	6.42	26.90	13.92	142	146
45.70	8.10	34.50	11.70	145	148
36.45	10.62	44.75	9.18	153	153
31.77	11.64	48.40	8.37	159	154
24.40	13.26	55.80	6.54	155	157

The glasses studied consisted of seven sodium silicates, eleven soda-barium glasses and six soda-lime glasses When the results of these measurements were plotted in a system in which the composition of the glass was represented by the abscissas and the surface tension by the ordinates, it was observed that the surface tension was roughly a linear function of the composition. It was therefore possible to compute the surface tension which each oxide showed in its combination in the glass, and with these factors to calculate the surface tension for the several glasses with the aid of the following formula:

$$T = a_1p_1 + a_2p_2 + a_3p_3, \text{ etc.},$$

in which T is the surface tension of the glass, a_1, a_2, a_3, etc., are the surface tensions of the several oxides and p_1, p_2, p_3, etc are the percentages of the respective oxides in the glass. The figures given in the tables

under "calculated" are the values of the surface tension obtained in this way, using the following factors

SiO_2	129
B_2O_3	45
BaO	195
CaO	323
Na_2O	160

In Table I are shown the results of measurements on sodium silicates. The first two columns show the composition of the glass; column three shows the observed and column four the calculated surface tension.

Table II shows the data obtained with the soda-barium glasses, and Table III that for the soda-lime glasses. In both of these tables the first three columns give the composition of the glasses and the last two columns give respectively the observed and calculated value of the surface tension. In Table IV are shown some soda barium glasses containing boric oxide. This series of glasses is especially interesting since it permitted a very wide range in the proportions of the several oxides and offered a severe test for the validity of the additive nature of surface tension.

In the measurements, in the tables given above, it is found that the observed and calculated surface tensions differ, for the most part, by not more than two or three per cent. This is not surprising since the surface tensions of liquids are, as a rule, very sensitive to the presence of small amounts of impurities. The glasses doubtless contain aluminum silicates and other impurities taken up from the crucible, which may perhaps affect the surface tension quite out of proportion to the amount present. The experimental error is not large when ten or more fibers are employed, as shown by the following measurements which were repeated, unknown to the worker, after several other glasses had been investigated. No. 1 is the second of the alkali silicates, as given in Table I and No. 2 is the last one of the same table.

	a	T.
1	45.4	141.6
	45.1	140.8
2.	43.7	136.3
	43.8	136.6

On comparing the values of the surface tensions of the pure oxides, as calculated from that of the glasses, we find in general that the acid-forming oxides, SiO_2 and B_2O_3, show lower surface tensions than the basic oxides. Placed in descending order they are as follows: CaO, 323; NaO, 195; Na_2O, 160; SiO_2, 129; B_2O_3, 45.

It is interesting to note that this surface tension of B_2O_3 is the same as that obtained by direct measurement on the fused boric oxide, and a little over one-half of that given by Quincke[1] (84.5). Inasmuch as the surface tensions of the lead borates previously described[2] do not show any regular relationship, this coincidence in the two values of the surface tension of boric oxide probably has little significance.

In conclusion, the writer desires to acknowledge his indebtedness to Mr. J. D. Malcolmson for his generous assistance in these measurements.

SUMMARY.

1. The surface tension of a number of soda-lime, soda-barium silicate glasses and of some soda-barium borosilicate glasses has been measured.

2. The surface tension of glasses is roughly a linear function of their composition.

3. The surface tension of silicate and borosilicate glass may be calculated with a fair degree of accuracy from the chemical composition, using the following values for the surface tension of the oxides: SiO_2, 129; B_2O_3, 45; BaO, 195; CaO, 323; Na_2O, 160.

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[1] Quincke, *Pogg. Ann.*, **138**, 141 (1869)
[2] Tillotson, *loc. cit.*

THE DETECTION AND DETERMINATION OF CYANOGEN AND HYDROGEN CYANIDE.

By F. H. RHODES.

Received June 6, 1912.

The usual method for the detection and determination of cyanogen and hydrogen cyanide in the presence of each other is based upon the difference in the products of the reaction of cyanogen and of hydrogen cyanide with a solution of potassium hydroxide. When passed into a solution of potassium hydroxide, hydrogen cyanide is quantitatively converted into potassium cyanide, whereas cyanogen forms equimolecular amounts of potassium cyanide and potassium cyanate.

The usual method for the detection of cyanogen in the presence of hydrogen cyanide consists in absorbing the gases in a solution of potassium hydroxide and testing for potassium cyanate. Potassium cyanate may be detected by acidifying the solution, heating to hydrolyze the cyanic acid liberated by this acidification, and testing for the ammonia formed by this hydrolysis.

The customary method for the determination of cyanogen in the presence of hydrogen cyanide is based upon the same reactions as the qualitative method just described. The gases are absorbed in a solution of potassium hydroxide, the potassium cyanate is decomposed by the addition of an excess of a strong acid, and the resulting ammonia is determined by the addition of an excess of alkali and distillation into standard acid. Both the qualitative and quantitative methods just described are tedious, and are liable to error because of the possibility of the formation of some ammonia by the simultaneous hydrolysis of some of the hydrocyanic acid liberated upon the acidification of the solution containing potassium cyanide.

Wallis[1] states that when hydrogen cyanide is passed into an acidified solution of silver nitrate it reacts quantitatively with the silver nitrate to precipitate silver cyanide. He also states that cyanogen does not react with an acidified solution of silver nitrate, and that any cyanogen which dissolves as such in the reagent may be removed practically completely by passing a current of air through the solution. Upon this difference of behavior of cyanogen and of hydrogen cyanide toward silver nitrate, Wallis based a method for the detection of cyanogen and of hydrogen cyanide when these gases are present together in a gas mixture, but he carried the work no further than to show the

[1] Wallis, *Ann. Chem.*, **345**, 353 (1906).

applicability of this method to the qualitative examination of a few special gas mixtures.

The present investigation was taken up to determine the applicability of the difference of behavior of cyanogen and hydrogen cyanide toward an acidified solution of silver nitrate to general qualitative gas analysis, and to ascertain whether this method could be used for the quantitative determination of cyanogen and hydrogen cyanide in the presence of each other.

The behavior of cyanogen when passed into a slightly acid solution of silver nitrate was first studied. Cyanogen was prepared by heating about two grams of mercuric cyanide in a hard glass tube. To one end of this tube was connected a series of four test tubes with side arm. In each of the first three of these absorption tubes was placed 5 cc. of a standard solution of silver nitrate and one drop of dilute nitric acid; in the fourth tube was placed 10 cc. of a 2 *N* solution of potassium hydroxide. A slow current of air was passed through the apparatus and the tube containing the mercuric cyanide was heated to dull redness, the heating being continued until the mercuric cyanide was completely decomposed. The current of air was continued for about twenty minutes after the decomposition of the mercuric cyanide.

A slight white precipitate was formed in the first absorption tube, but no precipitate appeared in any of the other tubes. The fourth absorption tube was disconnected and a portion of the solution contained in it was treated with 10 cc. of a solution of ferrous sulphate and one drop of a solution of ferric chloride. After being allowed to stand for about five minutes, the solution was made slightly acid with sulphuric acid. A heavy blue precipitate indicated the presence of cyanide in the solution of potassium hydroxide. Another portion of the solution from the fourth absorption tube was made acid and heated for a few minutes to hydrolyze any cyanic acid present. The resulting solution was made alkaline with a considerable excess of potassium hydroxide and warmed. Ammonia was copiously evolved, thus proving the presence of a considerable amount of cyanate. This experiment demonstrated that cynaogen will readily pass through an acidified solution of silver nitrate.

To ascertain whether appreciable amounts of cyanogen are absorbed by the solution of silver nitrate, the second absorption tube was removed from the apparatus, and the solution of silver nitrate contained in it was filtered. After thoroughly washing the filter paper with very dilute nitric acid, the combined filtrate and wash water was titrated with a standard solution of potassium sulphocyanate, with 5 cc. of a saturated solution of ferric ammonium alum as an indicator. The results,

5 cc. original solution of $AgNO_3$ = 3.91 cc. KCNS.
Solution from tube 2 = 3.92 cc. KCNS.

showed that cyanogen is not absorbed by a solution of silver nitrate that contains a slight amount of free nitric acid.

To learn whether any cyanogen is held back by the solution of silver nitrate and is not removed by a current of air, the third absorption tube was disconnected and the solution of silver nitrate that it contained transferred to a small beaker. To the solution was added an amount of a 2 *N* solution of potassium hydroxide (chloride-free) slightly in excess of that required to precipitate all of the silver. After standing for about three minutes, the solution was made slightly acid, filtered, and the filter paper thoroughly washed with dilute nitric acid. The combined filtrate and wash-water was titrated with a standard solution of potassium sulphocyanate. The results were as follows:

5 cc. original solution = 3.91 cc. KCNS solution
Solution from tube 3 = 3.91 cc. KCNS solution

If any cyanogen had dissolved as such in the solution of silver nitrate and had not been removed by the passage of the current of air through the solution, it would have reacted with the potassium hydroxide to form potassium cyanate and potassium cyanide, and the latter substance would have reacted with the silver nitrate to form insoluble silver cyanide. The fact that the amount of silver in solution was unchanged by the passage of a considerable amount of cyanogen through the reagent proves that any cyanogen that may dissolve as such in the slightly acidified solution of silver nitrate may be completely removed by the passage of a current of air through the liquid.

The slight precipitate obtained in the first absorption tube was due to the fact that the gas generated by the heating of the mercuric cyanide was not pure cyanogen, but contained small amounts of hydrogen cyanide. That this precipitate was not due to cyanogen is shown by the fact that there was no precipitate in either of the other absorption tubes containing acidified solutions of silver nitrate.

The completeness and rapidity of the absorption of hydrogen cyanide by a slightly acid solution of silver nitrate was next investigated. The hydrogen cyanide was generated by the action of an excess of dilute sulphuric acid upon 0.2452 gram of 96.15 per cent. potassium cyanide, and was passed through a series of four absorption tubes. In each of the first three of the absorption tubes was placed 15 cc. of an approximately *N*/10 solution of silver nitrate acidified with one drop of dilute nitric acid, while the fourth absorption tube contained 10 cc. of a *N*/2 solution of potassium hydroxide. After the complete decomposition of the potassium cyanide by the acid, a current of air was passed through the apparatus to sweep out any hydrogen cyanide remaining in the tubes. A precipitate appeared in each of the tubes containing silver nitrate. As far as could be judged from the volume of the precipitate, the precipitation of the silver in the first tube was almost complete before any precipitate appeared in the second tube. The precipitation in the third tube was slight, and did not begin until the precipitation in the second tube was almost complete. The fourth absorption tube was disconnected and the solution contained in it tested for cyanides by adding 10 cc. of a solution of ferrous sulphate and one drop of a solution of ferric chloride, allowing the solution and precipitate to stand for fifteen minutes, and then adding a slight excess of sulphuric acid. There was produced no blue pre-

cipitate of green color which showed that hydrogen cyanide is rapidly and quantitatively absorbed by a slightly acid solution of silver nitrate.

Upon the basis of the foregoing observations the following method for the detection of cyanogen in the presence of hydrogen cyanide was developed:

Two absorption tubes of the form already mentioned, the first containing 10 cc. of a 10 per cent. solution of silver nitrate, and one drop of dilute ($N/6$) nitric acid, and the second 10 cc. of a $N/2$ solution of potassium hydroxide, are connected in series and the gas mixture is passed through these tubes. This is followed by a slow current of air, the passage of which is continued for about 10 minutes. The absorption tube containing the solution of potassium hydroxide is then disconnected, and 5 cc. of a solution of ferrous sulphate and one drop of a solution of ferric chloride are added to the contents of the tube. After about 15 minutes there is added dilute sulphuric acid sufficient to dissolve the precipitated ferrous and ferric hydroxides. The appearance of a blue precipitate or of a distinct green color in the solution after acidification proves the presence of cyanogen in the original gas mixture.

The delicacy of this method was ascertained by passing known amounts of cyanogen gas through the absorbent. Since the cyanogen that is generated by heating mercuric cyanide was found to contain considerable amounts of hydrogen cyanide, the gas used in this test was generated by the action of a warm concentrated solution of cupric sulphate upon potassium cyanide. The cyanogen was collected in small glass tubes that were closed at each end with a stopcock. The volume of each of these small containers was previously determined by filling the tubes and the bore of the stopcocks with mercury, and then weighing the mercury. Several of these collection tubes were filled with cyanogen by connecting them in series and passing through them a current of cyanogen gas freed from hydrogen cyanide by passage through a slightly acid solution of silver nitrate, and dried by passage through a U-tube containing calcium chloride. The current of cyanogen through the tube was continued until the gas issuing from the last tube was completely absorbed by a solution of potassium hydroxide which showed that all air in the apparatus had been displaced. The stopcocks of the tubes were then closed, the tubes disconnected and any cyanogen remaining in the open end of the tubes blown out with air.

The delicacy of the test for cyanogen was then ascertained by connecting one of the above sample tubes with the absorption tubes containing solutions of silver nitrate and potassium hydroxide, and passing the gas through these tubes in the manner above described. The results of these qualitative tests were as follows:

Volume of cyanogen, Cc	Color developed
10	Blue precipitate
5	Blue precipitate
1	Blue precipitate
0.4	Green color
0.3	Faint green color
0.2	Very faint green color

From the above data it appears that as small an amount as 0.3 cc. of cyanogen may be detected in this manner. That the presence of hydrogen cyanide in the gas does not interfere with the delicacy of this method was demonstrated by passing through the absorbents a mixture of 0.4 cc. of cyanogen and 10 cc. of hydrogen cyanide and obtaining a distinct reaction for cyanogen under these conditions.

Since potassium cyanide is hydrolyzed to a considerable degree in aqueous solution with the formation of hydrocyanic acid, it was thought possible that the passage of a large volume of air through the apparatus might carry with it some of the hydrogen cyanide and thus decrease the delicacy of the test. It was found, however, that this was not the case, 0.4 cc. of cyanogen still yielding a distinct reaction when 20 liters of air was passed through the apparatus subsequent to the introduction of the cyanogen.

A small amount of carbon dioxide in the gas mixture under examination does not interfere with the test for cyanogen, but if an amount of gas containing carbon dioxide sufficient to convert all of the potassium hydroxide into potassium carbonate is passed through the reagent, naturally the reaction for cyanogen is then not obtained.

The presence of hydrogen cyanide in the original gas mixture is detected by collecting on a filter any precipitate that may have formed in the solution of silver nitrate in the first absorption tube, washing the precipitate with very dilute nitric acid, drying it, transferring it to a small sublimation tube, and warming it with a small amount of iodine (five milligrams or less. The formation of a sublimate of cyanogen iodide on the side of the tube proves the presence of silver cyanide in the precipitate and consequently of hydrogen cyanide in the original gas mixture: 0.1 mg. of silver cyanide, equivalent to 0.02 mg. of hydrogen cyanide, may be detected in this manner.

Experiments were next carried out to ascertain whether the difference in behavior of cyanogen and hydrogen cyanide toward a slightly acid solution of silver nitrate could successfully be utilized in the quantitative separation and determination of these two gases in the presence of each other. To this end a mixture of hydrogen cyanide and cyanogen was generated by the action of an *acidified* solution of copper sulphate upon potassium cyanide, and the gas mixture was collected in the tube containers described above. One of these containers was then connected in series with four absorption tubes, each of the first two of the tubes containing 5 cc. of a standardized (approximately $N/10$) solution of silver nitrate and one drop of dilute nitric acid. The third absorption tube contained 10 cc. of an approximately $N/2$ solution of potassium hydroxide free from chloride, and the last tube contained 5 cc. of this solution. The mixture of gases in the collection tube was driven through this absorption apparatus by a slow current of air which was continued for about 30 minutes. The first two absorption tubes were then disconnected and the solution of silver nitrate that they contained was transferred into a beaker and filtered. The precipitate and filter paper were washed with very dilute nitric

acid until free from soluble silver salts. The filtrate and wash water were then combined and titrated with a standardized solution of ammonium sulphocyanate (using ammonium-ferric alum as indicator) and the amount of hydrogen cyanide present in the original gas mixture calculated from the volume of ammonium sulphocyanate used.

The contents of the third and fourth absorption tubes was transferred into a beaker and a known volume of a standardized solution of silver nitrate added. The silver nitrate must be in excess of the amount required to precipitate all of the potassium cyanide in the solution as silver cyanide. The solution and the suspended precipitate were then thoroughly stirred, and dilute nitric acid added until the precipitated silver oxide redissolved and the solution became slightly acid. The precipitate of silver cyanide was now filtered off; precipitate and filter paper were washed with very dilute nitric acid until all soluble silver salts were removed, and the filtrate and wash water combined and titrated with a standardized solution of ammonium sulphocyanate using ammonium-ferric alum as indicator. The cyanogen present in the original gas mixture was then calculated, the reactions involved in the calculation being:

$$(CN)_2 + 2KOH = KCN + KCNO + H_2O.$$
$$KCN + AgNO_3 = AgCN + KNO_3.$$
$$AgNO_3 + KCNS = AgCNS + KNO_3.$$

The results of some determinations of cyanogen and hydrogen cyanide are given in the following table, the analyses being expressed in terms of the ratio of hydrogen cyanide to cyanogen by weight because by this means mistakes arising either from error in the determination of the volume of the small containing tubes or from the presence of gases other than cyanogen or hydrogen cyanide in the gas mixture are eliminated.

Tube.	Weight HCN.	Weight $(CN)_2$.	Ratio.
	Mixture No. 1.		
1	0.0177	0.009005	1.96 : 1
2	0.00586	0.00296	1.98 : 1
	Mixture No. 2.		
1	0.00134	0.0116	1 : 8.65
2	0.00044	0.0038	1 : 8.63

The results of the investigation may be summarized as follows:

1. Hydrogen cyanide is rapidly and quantitatively absorbed by a slightly acid solution of silver nitrate with the formation of silver cyanide.

2. Cyanogen is not absorbed by a slightly acid solution of silver nitrate and any cyanogen that may be dissolved as such in the solution is quantitatively removed when a current of air is passed through the liquid

3. Cyanogen may be detected in the presence of hydrogen cyanide even when the total volume of cyanogen in the gas mixture is as small as 0.3 cc. The method is applicable to the detection of small amounts of cyanogen in the presence of hydrogen cyanide and large volumes of air.

4. Hydrogen cyanide and cyanogen may be determined rapidly and accurately in the presence of each other.

I wish to express my indebtedness to Professor Dennis for the assistance and encouragement that he has given me in this work.

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RAPID AND ACCURATE METHODS FOR DETERMINING PHENOL.

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Received July 3, 1912.

In 1871 Landolt[1] made the first successful attempt to determine phenol quantitatively by precipitation as tribromphenol, and since that time numerous attempts have been made to obtain an accurate and easy method of determining phenol each experimenter working under varying conditions to suit his particular purpose. As a result of these investigations, many methods have been submitted for which claims of more or less accuracy and rapidity have been asserted. The time of the reaction period in most cases is too long for rapid determination.

A method has been suggested by Lloyd[2] in which he substitutes a hypobromite solution for Koppeschaar's[3] bromide-bromate solution. In his paper he shows that the tribromphenol is formed almost instantaneously and quantitatively (and that the time of the reaction period is reduced practically to zero). This hypobromite method has been adversely criticized by Olivier,[4] who in 1909 and 1910 published results which do not agree with Lloyd's. He did not find as high a percentage of error when a large excess of hypobromite was added to the phenol as did Lloyd, and he doubts the accuracy of Lloyd's numbers and methods. He shows also that the length of time required for Koppeschaar's method, using a bromide-bromate solution, may be reduced from one-half hour to nine minutes.

More recently, Wilkie[5] has published a method for the rapid determination of phenol, in which he used iodine in cold sodium carbonate solution. The reaction period for this method is 5–10 minutes. It has the disadvantage of requiring that the iodine solution be restandardized each time a phenol determination is made.

A more complete bibliography on phenol determination may be found in Lloyd's[2] paper of 1905 or Wilkie's papers of 1911–1912.

Our object in undertaking this research was to shorten if possible the time required for a determination of phenol by the bromide-bromate method and compare the hypobromite method with the bromide-bromate method for accuracy, ease of manipulation and time required for a determination.

Apparatus.—The apparatus used consisted of a shaking machine driven by a water motor, several five-liter bottles fitted with glass siphons, D. R. burettes and one-half liter ground stoppered bottles from the common stock in which the phenol determinations were made.

[1] *Berichte*, **4**, 770 (1871).
[2] *J. Am. Chem. Soc.*, **27**, 16 (1905).
[3] *Z. Ann. Chem.*, **16**, 233 (1876).
[4] *Rec. Trav. Chim.*, **28**, 362 (1909).
[5] *J. Soc. Chem. Ind.*, **30**, 399 (1911).

The shaking machine is a long, narrow and shallow wooden box 15 cm. × 9 cm. × 9 cm. inside measurements lined on the inside with felt covered pads. This box holds twelve one-half-liter bottles. The trough is fitted at one end with a grooved pulley two feet in diameter. At the center of this pulley and also at the center of the box on the end opposite the pulley are steel spindles which fit into the wooden bearings on the supporting frame. The frame is so constructed that this box may be removed and a larger or smaller box substituted. It was possible to rotate the shaker four revolutions per second, but one revolution per second was sufficient.

When a determination was to be made, each of the solutions was run into a 500 cc. bottle. The stoppers were then placed in the bottles and while being pressed inward were given a short sharp twist. This twist brought the two ground glass surfaces together and made it impossible for any of the solution to leak out or for the stopper to be thrown out when revolved rapidly.

The bottle was inserted between the padded sides of the box. The pressure of the pads held the bottles in firmly. By this construction no clamps are needed to hold the stoppers in the bottles during the time of shaking and the bottles are held in the machine by the pressure of the felt pads, no straps or clamps of any kind being used. This is an advantage, since, by eliminating all clamps, much time and labor, which are important factors when time determinations of small duration are being made, are saved.

In our investigations we made a total of two hundred determinations for which the machine was used and in no case did we experience any trouble or lose a determination on account of bottles flying out or stoppers leaking.

A photograph of the shaking machine appears below.

Solutions Used.—The solutions used in the determinations were approximately 0.1 *N* solutions of sodium thiosulphate, potassium hypobromite, a mixture of sodium bromide and bromate and phenol, concentrated hydrochloric acid (sp. gr. 1.2), a 20 per cent. potassium iodide solution and a starch solution used as an indicator.

The thiosulphate solution was prepared by dissolving 125 grams of sodium thiosulphate ($Na_2S_2O_3.5H_2O$) in five liters of water; 40 grams of liquid bromine dissolved in five liters of *N*/4 potassium hydroxide made up the hypobromite solution and the bromide-bromate solution consisted of 3.5 grams of potassium bromate and 55 grams of KBr per liter. The phenol solution for testing was made from the third distillation at 181.2° C. of Merck's c. p. phenol, 1.46 grams being diluted to 1 liter.

THE HYPOBROMITE METHOD.

In each of the following tables, the order given from left to right is the same order in which the solutions were added for the determinations. The tables show in each case the total volume, the volumes of phenol, hypobromite, hydrochloric acid, potassium iodide and thiosulphate used, and also the time of shaking and the percentage of the phenol present which were determined by means of this method.

Table I was prepared in order to determine the effect of time of shaking upon the results obtained, when the total dilution, volume of phenol and volume of hypobromite solution are kept constant and the solution is acid.

The method was as follows: Into a half-liter bottle containing 61 cc. water the following solutions were added in the order given: Five cc. of HCl (sp. gr. 1.2), 15 cc. of 0.1 *N* phenol and 19 cc. of 0.1 *N* hypobromite solution. The stopper was then inserted into the bottle and the latter placed in the shaker where it remained revolving for the desired length of time. After shaking, it was removed; 5 cc. of KI (20 per cent.) solution was added to the mixture and the bottle was returned to the shaker where it revolved for at least three minutes.

The following table shows the results obtained for one minute to one hour's shaking (the reaction period) before the KI solution was added.

TABLE I.—HYPOBROMITE.

No.	H_2O.	HCl.	C_6H_5OH.	KOBr.	Time. Min.	KI.	Time. Min.	$Na_2S_2O_3$.	Per cent. Phenol.
1*a*	61	5	15	19	1	5	3	3.99	100.3
1*b*	61	5	15	19	1	5	3	3.98	100.4
2*a*	61	5	15	19	5	5	3	3.97	99.7
2*b*	61	5	15	20	5	5	3	4.98	99.9
3*a*	61	5	15	19	10	5	3	3.88	100.5
3*b*	61	5	15	19	10	5	3	3.97	99.9
4*a*	61	5	15	19	15	5	3	3.89	100.4
4*b*	61	5	15	19	15	5	3	3.90	100.3
5*a*	61	5	15	19	20	5	3	3.91	100.3
5*b*	61	5	15	17	20	5	3	1.90	100.2
6*a*	61	5	15	19	30	5	3	3.88	100.5
7*a*	61	5	15	19	60	5	3	3.86	100.6
7*b*	61	5	15	19	60	5	3	3.91	100.2

Solutions.

Phenol.....	0.1022 N	KI	20 per cent.
KOBr.....	0.1016 N	HCl	1.2 sp. gr.
Thiosulphate.....	0.1003 N		

The above results indicate that the time of shaking has very little effect upon the percentages of phenol as determined. It will be noticed that the values for one minute's shaking are as correct as those for one hour. There is no result in the table which varies from the correct value by more than 0.6 of 1 per cent. and the average varies by 0.2 per cent. This is the degree of accuracy claimed by Lloyd for the hypobromite method.

In Table II are given the results obtained when the concentration of phenol with respect to the total

volume was varied but the relative concentrations of phenol and hypobromite were kept constant. In each case the time of shaking was 1 minute and the total dilution 100 cc.

TABLE II.

No.	H_2O.	HCl.	C_6H_5OH.	KOBr.	Time. Min.	KI.	Time. Min.	$Na_2S_2O_3$.	Per cent.
1*a*	61	5	15	19.0	1	5	3	3.97	100.14
1*b*	61	5	15	19.0	1	5	3	3.97	100.14
2*a*	83.5	5	5	6.5	1	5	3	1.50	99.79
2*b*	83.5	5	5	5.5	1	5	3	1.50	99.79
3*a*	90.4	5	3	3.9	1	5	3	0.92	99.14
3*b*	90.4	5	2	2.6	1	5	3	0.60	99.71
4*a*	92.7	5	1	1.3	1	5	3	0.32	98.90
4*b*	92.7	5	1	1.3	1	5	3	0.31	98.81

Solutions—See Table I.

The results obtained indicate that amounts of phenol as small as 0.000015 gram per cubic centimeter may be determined within 1 per cent. by this method and with a reaction period of one minute.

Table III shows that shaking for one minute is sufficient by the method used for an accuracy not greater than four parts per thousand. Each test was run with a total volume of 100 cc. and in each the concentrations of the various solutions were the same. The six determinations were a single series. All six are submitted, none rejected, thus giving a fair estimate of the amount of the error to be expected generally in a laboratory determination.

TABLE III.—HYPOBROMITE.

No.	H_2O.	HCl.	C_6H_5OH.	KOBr.	Time. Min.	KI.	Time. Min.	$Na_2S_2O_3$.	Per cent.
1	61	5	15	19	1	5	3	3.99	100.3
2	61	5	15	19	1	5	3	3.98	100.4
3	61	5	15	19	1	5	3	4.02	99.6
4	61	5	15	19	1	5	3	4.00	99.8
5	61	5	15	19	1	5	3	4.01	99.7
6	61	5	15	20	1	5	3	5.00	99.8

Solutions—See Table I.

Attention is called to the fact that in each of these tables, the phenol was first diluted with water before the hypobromite solution was added to it. *This* is of interest because of the fact that a number of authors state that in the determination of phenol by bromine,[1] a red compound is formed in the white precipitate which is probably tetrabromphenoquinone. Only once or twice in all our determinations did the precipitate show even a light pink shade, never yellow which would indicate tribromphenol bromide, and in all the other cases the precipitate was perfectly white. In every case where the red compound is mentioned the phenol solution was used with greater concentration than $N/100$; it was found that diluting the phenol to approximately $N/100$ reduced the formation of this compound to zero and possibly increased the accuracy of this method.

The Permanency of a Hypobromite Solution.—In estimating phenol, conflicting determinations were obtained by us when it was assumed that a fresh hypobromite solution retains a constant quantity of available bromine. Allen[2] states that a hypobromite solution made alkaline by dissolving 62.2 grams of pure NaOH (this is 50 per cent. more caustic than is necessary to react with the bromine according to the equation, $Br_2 + 2NaOH = 2NaBrO + H_2O$) and made up to 0.16075 N loses not more than 0.8 per cent. of its bromine by boiling it for one hour. Lloyd[1] assumes from Allen's paper that the available bromine in a solution of hypobromite is fairly constant. This is true if the bottle is kept full of solution and corked with a ground stopper. But if the ordinary 5-liter bottle be fitted up with a paraffined bark cork, siphon and inlet for air, the hypobromite solution changes its strength. A fresh solution made up in this laboratory by dissolving 8 grams of bromine per liter in N 4 KOH changed its strength in thirty-two days from 0.0865 N to 0.0781 N, a decrease 0.3 per cent. strength per day. A second fresh solution of strength 0.1654 N changed in 12 days to 0.1584 N, that is a change of 0.33 per cent. per day. A third solution, which was kept in a ground stoppered brown glass bottle in a dark compartment, changed from 0.1346 N to 0.1340 N in fifty-seven days. It is evident that this solution, which was quite yellow and smelled of free bromine, retained its strength when kept well corked in a brown glass bottle. This may account for the conflicting statements made regarding available bromine in a hypobromite solution. Owing to the possibility of bromine evaporating from a strongly alkaline hypobromite solution it is necessary to test this strength of hypobromite after each determination if these are more than a few hours apart, especially if the solution has an inlet for air to allow the siphon to operate, or if the bottle is badly corked.

The Acidity of the Phenol Hypobromite Solution.—It is imperative, if hypobromite is used in determining a phenol solution as tribromphenol, to have the solution acid both before and after the hypobromite is added. Otherwise the phenol ring is broken[2] up in alkaline hypobromite and passes over into carbon tetrabromide and possibly higher homologues.

TABLE IV.—ALKALINE PHENOL HYPOBROMITE

No.	H_2O.	C_6H_5OH.	KOBr.	Time.	HCl.	KI.	Time. Min.	$Na_2S_2O_3$.	Per cent.
I*a*	64.5	2.5	18	1 min.	5	5	3	19.81	167.84
II*a*	64.5	2.5	18	1 min.	5	5	3	19.78	169.01
I*c*	64.5	2.5	18	5 mins.	5	5	3	19.04	197.25
II*c*	64.5	2.5	18	5 mins.	5	5	3	19.06	196.86
I*d*	64.5	2.5	18	10 mins.	5	5	3	18.96	200.39
II*d*	64.5	2.5	18	10 mins.	5	5	3	18.94	201.17
I*e*	64.5	2.5	18	20 mins.	5	5	3	18.90	202.74
II*e*	64.5	2.5	18	20 mins.	5	5	3	18.89	203.13
I*g*	64.5	2.5	18	1 hr.	5	5	3	18.79	205.49
II*g*	64.5	2.5	18	1 hr.	5	5	3	18.76	208.22
I*i*	64.5	2.5	18	18 hrs.	5	5	3	18.08	234.51
II*i*	64.5	2.5	18	18 hrs.	5	5	3	18.07	234.90

Solutions.

Phenol	0.1022 N	KI	20 per cent
KOBr	0.1318 N	HCl	1.2 sp. gr.
Thiosulphate	0.09816 N		
18 cc. 0.1318 N KOBr	= 23.72 cc. 0.1 N KOBr		
2.5 cc. 0.1022 N phenol	= 2.55 cc. 0.1 N phenol		

In Table IV the acid was not added until after the hypobromite. Column 5 shows the time during which the solution was alkaline. The table shows the rate at which the bromine is used up in an alkaline phenol solution. The last column gives the per cent. of Br disappearing, calculating as 100 per cent. the amount of Br required to form tribromphenol, when the solution is acid.

[1] Beckurts, *Arch. Pharm.*, **5**, 24, 561 (1886); from *J. Soc. Chem. Ind.*, **5**, 5, 546 (1886).

[2] *J. Soc. Chem. Ind.*, **3**, 65 (1884).

[1] *J. Am. Chem. Soc.*, **27**, 10 (1905).

[2] Olivier, *Rec. Trav. Chim.*, **29**, 294 (1910); Colhe, *J. Soc. Chem. Ind.*, p. 264 (1894); Wallach, *Ann. Chem.*, **275**, 147 (1893); **159**, 322.

The above table indicates that if the solution be alkaline for only one minute after the hypobromite is added, an error as great as 67 per cent. may be introduced in the determination, and a longer period gives a greater error. Lloyd uses sufficient acid to keep the solution strongly acid although he does not mention the attendant danger if the solution were alkaline. Olivier[1] rather inconsistently expresses surprise at the amount of acid used by Lloyd and at the same time shows that if the solution become alkaline an error of 125 per cent. may be introduced in a single determination.

It may be noted that no precipitates appeared after adding the acid.

THE BROMIDE-BROMATE METHOD.

This method is similar in many respects to the hypobromite method. Instead of using a solution of hypobromite as in the first case, a solution consisting of a mixture of potassium bromide and potassium bromate (Koppeschaar's solution) was used. This is the standard solution used by the United States Pharmacopoeia and is made as follows: 3.5 grams of potassium bromate and 55 grams of potassium bromide are dissolved in water and then diluted up to 1 liter.

This solution has considerable advantage over the hypobromite solution in that it contains no free bromine and therefore does not have the objectionable odor of the hypobromite solution. For the same reason, it is much more stable than this solution[2] and does not require to be standardized with each operation. The chief objection to the use of the bromide-bromate solution, however, has been that it was too slow. Koppeschaar recommends 15 minutes shaking and the U. S. P. 30 minutes, before the KI solution is added.

As shown by the following tables it is not necessary to shake for one-half hour to obtain an accuracy of three parts per thousand. The order of adding the solutions is shown in each table reading from left to right.

TABLE V.—BROMIDE BROMATE.

No.	H_2O.	HCl.	C_6H_5OH.	Bromide bromate.	Time. Min.	KI.	Time. Min.	$Na_2S_2O_3$.	Per cent.
1*a*	61	5	15	19	1	5	3	2.80	99.72
1*b*	61	5	15	19	1	5	3	2.75	100.04
2*a*	61	5	15	19	5	5	3	2.80	99.72
2*b*	61	5	15	19	5	5	3	2.77	99.92
3*a*	61	5	15	19	10	5	3	2.80	99.72
3*b*	61	5	15	19	10	5	3	2.79	99.79
4*a*	61	5	15	19	15	5	3	2.78	99.85
4*b*	61	5	15	19	15	5	3	2.77	99.92
5*a*	61	5	15	19	20	5	3	2.73	100.11
5*b*	61	5	15	19	20	5	3	2.80	99.72
5*c*	61	5	15	19	20	5	3	2.75	100.04
5*b*	61	5	15	19	20	5	3	2.82	99.60
6*a*	61	5	15	19	30	5	3	2.70	100.30
6*b*	61	5	15	19	30	5	3	2.74	100.11
7*a*	61	5	15	19	60	5	3	2.70	100.30
7*b*	61	5	15	19	60	5	3	2.71	100.30

Solutions.

Phenol..... 0.1022 N KI 20 per cent.
Bromide bromate 0.09493 N HCl 1.2 sp. gr.
Thiosulphate.... 0.09816 N

Table V was prepared to determine the effect of time of shaking upon the results obtained when the total dilution, volume of phenol and volume of bromide bromate are kept constant and the solution acid.

In Table V the constant volumes of water, phenol, acid and bromide-bromate solution were used, but the time of shaking varied. It will be noticed that for no test was there a greater error than 0.6 per cent. and that with one exception all the results are within 0.3 per cent. The results obtained for one minute's shaking are as accurate as those for 15 minutes, 30 minutes and 1 hour.

In order to confirm the one-minute determinations, a series of five tests were run exactly similar to those in Table V. The five results are submitted, none rejected, thereby giving an idea of the magnitude of the errors to be expected in an ordinary laboratory determination by this method.

The results given below in Table VI show an average error of 0.3 per cent., the greatest error being 0.4 per cent. for a reaction period of only 1 minute.

TABLE VI.—BROMIDE BROMATE.

No.	H_2O.	HCl.	C_6H_5OH.	Bromide bromate.	Time. Min.	KI.	Time. Min.	$Na_2S_2O_3$.	Per cent.
1	61	5	15	20	1	5	3	5.81	100.4
2	61	5	15	18	1	5	3	3.88	100.4
3	61	5	15	18	1	5	3	3.90	100.2
4	61	5	15	18	1	5	3	3.92	100.3
5	61	5	15	18	1	5	3	3.90	100.2

Solutions.

Phenol..... 0.08815 N KI 20 per cent.
Bromide bromate 0.09493 N HCl 1.2 sp. gr.
Thiosulphate.. 0.09816 N

Table VII like Table II varies the concentration of phenol with respect to the total volume, but keeps the relative quantity of bromide bromate with respect to the phenol constant. In this table the time of shaking was taken as one-half hour. This length of time was chosen according to the U. S. P., as Table VII was completed before Tables IV and V.

TABLE VII.—BROMIDE BROMATE.

No.	H_2O.	HCl.	C_6H_5OH.	Bromide bromate.	Time. Min.	KI.	Time. Min.	$Na_2S_2O_3$.	Per cent.
1*a*	61.	5	15	19.	30	5	3	2.70	100.36
1*b*	61.	5	15	19.	30	5	3	2.74	100.11
2*a*	72.	5	10	13.	30	5	3	2.12	100.39
2*b*	72.	5	10	13.	30	5	3	2.15	100.10
3*a*	83.5	5	5	6.5	30	5	3	1.02	101.15
3*b*	83.5	5	5	6.5	30	5	3	1.08	100.00
4*a*	90.4	5	2	2.6	30	5	3	0.39	102.02
4*b*	90.4	5	2	2.6	30	5	3	0.43	100.05
5*a*	92.7	5	1	1.3	30	5	3	0.19	102.50
5*b*	92.7	5	1	1.3	30	5	3	0.21	100.58

Solutions—See Table V.

The results for 1 and 2 cc. of phenol are seen to be less concordant than those for larger amounts. However, as one drop is an error of 5 per cent. in 1 cc., and as the phenol solution was measured out from a burette and not weighed, the agreement is fairly good. The table shows that 0.000015 gram of phenol per cubic centimeter may be determined by this method with a maximum error of 2 per cent. The method is probably much more sensitive than this if more dilute solutions are used.

From these tables we have come to the following conclusions for work requiring an accuracy not closer than 0.3 per cent. *First*, it is not necessary to shake the acidified phenol solution with Koppeschaar's solution (bromide bromate) or with Lloyd's hypobromite solution for a longer time than one minute

[1] Olivier, *Rec. Trav. Chim.*, **29**, 294 (1910).

[2] See Part V, SUMMARY, page 659, also page 657.

if a continuous shaker is used. *Second*, if the conditions of dilution, etc., are those given in the preceding tables no red or yellow compounds are observed in the white tribromphenol precipitate.

In addition to the above experiments, tests were run by the two methods to determine the error which might be introduced in the determinations due to chemicals, evaporation of bromine due to the use of ordinary one-half liter bottles, methods of working, etc. Thus, an error might be introduced by running the hypobromite solution into the phenol without shaking if the region where the hypobromite was most concentrated became alkaline. Several tests were made to determine this, but no appreciable effect was noticed.

A series of six determinations to find the effect of titrating back with the thiosulphate after periods of 1, 2 and 3 minutes (continuous shaking) from the time when the KI was added, gave results which showed a maximum error of 0.5 per cent. within themselves. Accordingly an error of not more than 0.5 per cent. is introduced if the solution is shaken only 1 minute after adding the potassium iodide.

Blank experiments were run under the same conditions as the original determinations which showed that the maximum error introduced by the solutions, manipulation, bottles, etc., was 0.3 per cent.

Directions.—(1) $N/10$ sodium thiosulphate and a $N/10$ of either hypobromite or bromide bromate, 20 per cent. KI and $^1/_2$ per cent. starch solutions.

(2) Into a 500 cc. bottle, fitted with a ground glass stopper, put 60 cc. water, 5 cc. hydrochloric acid (sp. gr. 1.2) and then add 15 cc. of the unknown phenol solution which is to be determined and which has previously been diluted to about $N/10$. If the solution is weaker than $N/10$ no previous dilution is required. Add quickly enough $N/10$ hypobromite or bromide-bromate solution to make the solution yellow and then add in addition 10 per cent. of the amount already added. Place the stopper in the bottle and shake continuously for one minute. Add to the solution in the bottle 5 cc. potassium iodide solution (10 per cent.) and again shake for three minutes. Wash down the stopper and sides of the bottle and titrate the solution with the $N/10$ thiosulphate, using starch solution as an indicator. The starch must not be added until enough thiosulphate has been run in to make the solution almost colorless. The quantity of thiosulphate used represents the quantity of free iodine, and therefore the quantity of excess bromine. The difference between this quantity and the known quantity of bromine added gives the amount of solution present. Each cubic centimeter of $N/10$ bromine used up is equivalent to 0.00156 gram of phenol.

SUMMARY.

I. The results show that by the above methods of manipulation, either with the hypobromite or with the bromide-bromate solution, phenol determinations can be made within an error of 0.3 per cent. with only one minute of continuous shaking after the solution containing the bromine is added, *i. e.*, the reaction period may be reduced from 30 minutes to 1 minute without sacrificing accuracy.

II. The phenol in each case was diluted until it was approximately $N/100$ before the determination was made. The resulting precipitate with the hypobromite or bromide-bromate solution was white and flocculent in each case and the precipitate showed no traces of red tetrabromphenoquinone or yellow tribromphenol bromide.

III. In order to secure correct results, the phenol solution must be acid after the bromine is added. If it is alkaline, an error is introduced which increases as the concentration of the phenol in the solution diminishes and the reaction period increases.

IV. The error introduced by shaking the solution for only one minute after the KI solution is added before titrating back with thiosulphate is 0.5 per cent. Three minutes shaking eliminates this error and longer shaking has no effect.

V. The bromide-bromate solution has the advantage over the hypobromite of being permanent. When the solution used was first made, its strength was 0.09493 N. After three months duplicate tests gave 0.09495 N The hypobromite solution weakened one-third per cent. every twenty-four hours for the first few days after the solution was made. The bromide-bromate solution has not the unpleasant odor or free bromine.

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THE COLORIMETRIC DETERMINATION OF IRON IN LEAD AND ITS OXIDES.

By JOHN A. SCHAEFFER.

Received June 20, 1912.

The determination of the small percentage of iron always found in lead and its oxides must frequently be made by chemists working in industries where any appreciable amount of iron in raw materials has a deleterious effect on the finished product. This is especially true in the use of red lead and litharge in the manufacture of high-grade cut glass, and lead and its oxides in the manufacture of lead accumulators, where the determinations are constantly made The gravimetric determination of this constituent necessitates a lengthy and a more or less inaccurate analysis, owing to the many operations entailed. A volumetric determination is also in many cases not sufficiently accurate and rapid for estimating the very small percentages which are often present.

The following colorimetric method was developed to fill this need and it has been found that no other method compares with it in rapidity, ease of manipulation, or in accuracy for the estimation of the small percentages of the above constituent present in lead and its oxides. The method is a modification of Thomson's[1] method, so adapted as to be readily applied to the above mentioned analysis.

It is carried out in the following manner:

In the analysis of litharge or metallic lead, treat one gram of the sample in a beaker with 15 cc. of water

[1] *J. Chem. Soc.*, **1885**, 493.

and sufficient nitric acid to convert all the lead present to lead nitrate. Should there be any separation of basic lead nitrate add more water until complete solution is effected.

In the analysis of red lead, treat one gram of the sample with 10 cc. of water and sufficient nitric acid to convert all the oxide present, excepting the lead dioxide, to lead nitrate. Add 10 cc. of hydrogen peroxide (1 : 3.5) to the solution, and boil for a minute until all the oxides of lead pass into solution.

After complete solution of either the metallic lead, litharge or red lead, boil the nitrate solution gently for several minutes to convert all the iron to the ferric condition, cool the contents of the beaker, neutralize the free nitric acid present with ammonium hydroxide and render faintly acid with nitric acid. A solution made from red lead may, after neutralization and the subsequent addition of acid, show the presence of lead dioxide. When this occurs, the solution can be rendered clear by the addition of a few drops of the hydrogen peroxide solution.

Wash the contents of the beaker into a 100 cc. Nessler cylinder, add 15 cc. of dilute ammonium sulphocyanide (1 : 20) and dilute to the mark. The intensity of the blood-red color depends upon the amount of iron present. The color is compared with a blank made in the following manner:

A solution of ferric ammonium sulphate of known strength is required. This is made by dissolving 0.7022 gram of ferrous ammonium sulphate in water. Acidify with sulphuric acid, heat to boiling and add a solution of potassium permanganate until all the iron is converted to the ferric condition. Only the very slightest pink tinge may be present after the addition of the potassium permanganate, as this tinge will fade away, while the presence of a pink color tends to vitiate the results. Allow the solution to cool and dilute to one liter. One cc. of this solution equals 0.0001 gram of iron.

Prepare the blank by pouring into a 100 cc. Nessler cylinder 10 cc. of hydrogen peroxide of the above strength, provided hydrogen peroxide was added for the solution of the oxide, approximately the same amount of nitric acid as was required for the solution of the original metallic lead or oxide, and 15 cc. of ammonium sulphocyanide solution. Dilute to 100 cc. and titrate to the exact color developed in the sample under examination, by the addition of the standard ferric ammonium sulphate solution. One cc. of this solution equals 0.01 per cent. of iron when a one-gram sample is used. The percentage of iron present should not require more than 2 or 3 cc. of the standard to equal it, or the color will be too deep for comparison.

It will be found that the color can be accurately compared to within 0.001 per cent. of iron content. The small percentage of copper present in lead and its oxides does not interfere with the reaction.

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A RAPID MICROSCOPICAL METHOD FOR THE DETERMINATION OF ARSENIC, AS ORPIMENT, IN SHELLAC.[1]

By Robert Schwarz

Received July 15, 1912

As is well known, orpiment, the mineral form of arsenic trisulphid, is very generally added to shellac in India, where this product is collected and prepared for the market. Orpiment is added merely to make shellac more opaque and light straw-colored.

An attempt has therefore been made to obtain from India shellac to which no orpiment has been added, but it has been found that, for some unknown reason, almost all shipments of so-called "arsenic-free" goods contain from small amounts to considerable quantities of arsenic, mostly in the form of orpiment. Therefore it appeared advisable to develop a method of qualitatively determining orpiment in shellac, which method would be more rapid than the Gutzeit or Marsh tests. Such a method has been evolved and bases itself, (1) upon the fact that orpiment is insoluble in alcohol and can be precipitated from alcoholic solution of shellac by centrifugal motion, and (2), upon the characteristic appearance of orpiment under the microscope. When examined in this manner, orpiment appears as transparent to translucent granular masses and imperfect crystals of a distinctly characteristic yellow-greenish color.

The method, therefore, is very simple and rapid, as can be seen from the following:

A 10-gram average sample is ground fine in a coffee mill and then dissolved in 15 cc. of methyl alcohol, solution being hastened by shaking and warming the flask. The varnish is then poured into a graduated tapering tube and this revolved in a centrifugal machine for 5–6 minutes at 1000–1500 revolutions per minute. This causes the precipitation of the greater part of the insoluble material, which contains the orpiment. The varnish is then decanted, the precipitate shaken with methyl alcohol and the tube again revolved in the centrifuge for one to two minutes. The alcohol is then decanted as thoroughly as possible, the amount of the precipitate recorded, and a small portion transferred to a microscopic slide by means of a capillary tube. This preparation is then carefully examined under the microscope, using a magnification of 450–600 diameters.

With an ordinary brewers' shellac or varnish containing a normal amount of insoluble material and above 150 parts of arsenic per million, several pieces of orpiment will be observed in each field. Some shellacs, however, contain a considerable amount of insoluble material, and so the precipitate becomes larger and the number of pieces of orpiment in each field correspondingly smaller. The method has been used not only on the common grades of shellac, but it has also been tried on so-called "arsenic-free" shipments and three bleached shellacs. The results of all tests have been embodied in a table in which is given the number of each test, description of the sample, amount of the precipitate, number of pieces of orpiment

[1] Paper presented at the New York Section of the American Chemical Society, June 7, 1912.

found in each field or preparation, and the amount of arsenic trioxide, as determined by the Marsh or Gutzeit test. The Marsh or Gutzeit test determines the total amount of arsenic present, and therefore, as Langmuir and White[1] have shown that a certain amount of orpiment may be dissolved in the shellac in the process of manufacture, it is not surprising that in some instances the microscopic tests failed to reveal orpiment, while the chemical tests showed appreciable amounts of arsenic to be present.

Sample Number.	Description.		Sediment.	Orpiment crystals per field.	As_2O_3 Parts per million. M = Marsh G = Gutzeit.
1	Varnish	Orange	0.1 cc.	4–5	400 M
2	Varnish	Orange	0.05	1	60 M
3	Varnish	Orange	0.05	4–5	155 M
4	Varnish	Orange As free	0.025	none[1]	none G
5	Varnish	Manheim	none	none	none M
6	Varnish	Manheim	0.02	1–2	112 M
7	Varnish	White	0.05	none[1]	none G
8	Shellac	Grain Lac.	1.5	1	45 M
9	Shellac	R & P garnet	0.1	none[1]	85 M
10	Shellac	Gr orange	0.075	none[1]	none M
11	Shellac	Reg. orange	0.075	6–8	550 M
12	Com. As free shellac		0.025	1[2]	4 G
13	Com. As free shellac		0.05	1[2]	7.5 G
14	Com. As free shellac		0.025	2[2]	4 G
15	Com. As-free shellac	Grain lac.	1.00	1[2]	20 G
16	Com. As-free shellac	Grain lac.	1.00	1[2]	20 G
17	Bleached shellac	.....	0.01	1[2]	6 G
18	Bleached shellac	..	0.25	1[3]	traces G-M
19	Bleached shellac	.....	0.01	none[1]	.15 G

[1] Three preparations examined.
[2] Number of crystals in each preparation.
[3] One crystal in every third preparation.

It is easily seen from the above table that the sediment from a brewers' varnish (samples 1–6), which is generally made from the ordinary grades of shellac, contains such an amount of orpiment that there are always one or more crystals present in each microscopic field. Sample 4, however, did not show any orpiment in three microscopic preparations, and as experience had shown that this number of preparations would show at least one crystal of orpiment, if any were present, this sample was judged orpiment-free. The Gutzeit test showed that no arsenic in any form was present.

Of the raw or purified shellacs all but two showed crystals of orpiment where arsenic was subsequently found by the Marsh or Gutzeit tests. The two exceptions were No. 9, of which a number of preparations were made and no orpiment found, and No. 19, a bleached, wax-free sample, which gave similar results. It is quite probable that in both instances the arsenic was in solution, and that any orpiment which had been present in the raw lac had been removed in the process of manufacture.

Regarding samples Nos. 12–18, it is interesting to note that the method will show the presence of orpiment even when the total arsenic present is only 4 parts per million, and in one instance—sample No. 18—one crystal was found in every third microscopic preparation, while the Gutzeit and Marsh tests showed the presence of traces only of arsenic.

As regards using the method to obtain quantitative approximation of the amount of orpiment present, it must be stated that, in the first place, the method is suggested only as a qualitative test. However, by using the same microscope, ocular and objective, and by comparing the sediments of unknown shellacs with those of samples containing known amounts of orpiment, a fair idea of the amount of orpiment present can be obtained.

In conclusion I wish to acknowledge my indebtedness to Dr. A. C. Langmuir, at whose suggestion this paper was written, and who has given valuable advice in the preparation of the same.

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[1] *J. Soc. Chem. Ind.*, **1911**, 786

SOME PRACTICAL METHODS FOR TESTING AND IDENTIFYING COLORS FOR PRINTING INKS AND SIMILAR PIGMENTS.

By SAMUEL LEVINSON

Received May 27, 1912.

Every manufacturer, in fact every large user of colors, should be in position to identify and match colors brought to his attention as a producer, jobber or buyer. In this paper we shall consider only the so-called LAKE COLORS, *i. e.*, colors made from coal-tar dyestuffs consisting of the base, coloring matter and usually some substance or substances used to fasten the dye to the base. Analytical methods very often are insufficient to properly identify chemical preparations. A complete analysis giving the percentage of all the constituents which can be properly identified chemically will often be of comparatively little value. But on the other hand a synthetic test, *i. e.*, a combination of different materials which results in a substance identical with the one tested will make the examination complete and at the same time provide all the important analytical data. In very many cases the synthetic test is simpler and takes up much less time, than an analysis. In many factories where there are no or very limited laboratory facilities a complete analysis is out of the question and one must per force take refuge in synthetic methods. Certain conditions, of course, cannot be duplicated in the laboratory and besides the chemist must be familiar not only with analytical methods but must understand the manufacture of the articles in question. Happily in the color line conditions are such that almost any color can easily be prepared in the laboratory and the preparation requires but little time and very limited facilities.

It is relatively easy to find out the percentage of coloring matter in a color and in many instances the manufacturer will state the nature of the dye used, but, if the consumer should pay according to the percentage of dye, as revealed by such analysis, the results might prove disastrous. It is quite a common occurrence for two colors with exactly the same percentage of dye to show different strengths. In examining a new color it is worth while to remember that there are relatively few *lake colors* in the market in shades other than RED, because some of the more important INORGANIC colors, like chrome yellow, chrome green, ultramarine and prussian blue, are

much cheaper. So in many instances we can tell by the shade and price without any further examination, whether the article in question is a lake color or an inorganic color. The purpose for which the color is used is a factor of even greater importance; it is evidently useless to look for a heavy gritty base in a color intended for fine printing inks.

Very little apparatus and but few chemicals are required in order to form a definite idea of most of the colors. A few test tubes, a Bunsen burner, and an alcohol lamp will enable one to make most of the necessary tests. When matching is the more important part of the work it very often becomes necessary to make up counter samples, *i. e.*, a color having all or most of the important qualities of the submitted sample. For this work a few Mason jars of one quart capacity can be used as working tanks; glass rods, or even pieces of wood will serve as stirring rods; all the dissolving can be performed without the necessity of boiling by using hot water in enameled ware dishes. As most of the operations included in the manufacture of colors take place with the use of live steam, passing through open iron pipes with a maximum temperature of approximately 170° F., it will readily be seen that the use of boiling water will practically duplicate the working conditions in the manufacture.

Several glass funnels for filtration, or better still a suction pump and a drying oven will complete the outfit. In the absence of a drying oven a pot of boiling water covered with a piece of tin can be used for drying. A scale and a set of metric weights will be very convenient, as by figuring 1 gram to 9 cc. as the equivalent of a pound per gallon, it is easy to figure out the dimensions of tanks and vessels required for the actual manufacture. The concentration of the solutions of the materials used is a very important item in manufacture.

The color submitted for examination must be first examined as to the shade and strength. In order to do this properly it is very convenient to have a fair sized collection of standard samples, either prepared in the laboratory or standard market goods; the names of the manufacturers, trade names, prices, etc., should be carefully kept on record. The sample in question is "rubbed out" on a glass plate in some vehicle, either linseed oil, varnish, water or glue solution, depending on the use to which the color is to be put. This mixture is spread out in a thin layer alongside of a sample of some standard color rubbed out in exactly the same way, which appears to be nearest in shade. The two rub-outs can be placed together on a piece of glass. It is also very convenient to spread the colors on white paper, which should not be too heavy. Another method is to put separately very small masses of the colors in oil or varnish on a large palette knife and then rub them out together on a piece of paper in adjoining smears. In this way both the overtone and undertone can be studied and compared with standard samples.

The next in order is a strength test, or a determination of the staining power. For this the color is reduced with a given amount of an inert white base, rubbed out and compared with a standard exactly as before. For reducing I have always used oxide of zinc with very satisfactory results. The color is mixed with ten, twenty or in case of strong color even fifty or a hundred parts of white (by weight). The same concentration of the standard color is prepared. To facilitate matters it is very convenient to prepare dry mixtures of standard colors 1 : 10 or 1 : 20 and keep them in small bottles for further reference. If the shade of the sample and standard are identical and they differ in strength only, the addition of more zinc oxide will help to determine the exact strength. In the course of the above determinations we can also consider the general behavior of the color "bleeding" in oil, in water, resistance toward common reagents, acids and alkalies, etc. If the overtone, undertone, strength, and general behavior of two colors are alike they can be safely considered identical for all practical purposes.

If none of the standards on hand matches the sample it becomes necessary to examine the color more closely, beginning with the base. The specific gravity of the color will furnish a good clue in this matter, *e. g.*, a heavy color cannot be a lake made on alumina hydrate base. It must contain some of the heavier bases (barytes, clay, different lead salts, etc.). A few simple tests like the following will suffice to determine the base. A little of the color is treated in a test tube with hydrochloric acid; strong effervescence will show the presence of carbonates, usually either Paris white, or carbonate of barium or lead. The latter are both heavier than Paris white. The following test will clear up the question: A little of the color is boiled in a test tube with strong acetic acid and some hot water and a few drops of a solution of potassium iodide are added. The immediate formation of heavy golden crystals will show the presence of lead as a base, as previously confirmed by the heaviness of the color. If the crystals are formed very slowly, we can deduce that lead was used but in small quantities, evidently in order to fasten the dyestuff. The coloring matter can be easily destroyed by boiling the color with a mixture of hydrochloric and nitric acids. The filtrate is tested in the usual way for soluble metals. Large amounts of aluminium for instance will show that the color contains some hydrate of that metal. If a microscope having a magnification of about 100 is handy, it is very convenient to examine the color on a slide rubbed out with a little alcohol. In this way it is easy to determine the difference between barytes and blanc fixe which are identical chemically (natural and artificial sulfate of barium) but act quite differently as bases for colors.

After getting some idea of the base, we shall next proceed to examine the coloring matter proper. The presence of small quantities of lead previously determined in testing for this metal in the case of a red color usually bespeaks the presence of eosines; decided fluorescence of the color with alkalies will confirm it. It is however important to remember that some of the newer coal-tar products show quite a similar behavior; *e. g.*, Pigment Scarlet 3 B (of Meister, Lucius and

Bruening). A bromine test will prove the presence of eosines more positively and exclude Pigment Scarlet.

Having excluded this class of dyes, the identification of so-called Permanent Colors made with Paranitraniline is next in order. When treated with strong sulfuric acid this class shows a cherry-red reaction; boiled with alcoholic caustic soda solution a dark violet will appear. The above method has been used by the author for the last six years, and has been sufficient for the complete identification of this class of colors, nor has confusion with any other class ever occurred.

Using some of the most common reagents like sulfuric acid, hydrochloric acid, caustic soda, also alcoholic caustic soda, alcohol, etc., and comparing the resulting reactions with standard samples made with known coal-tar dyes, or even with the coal-tar dyes *per se*, we can arrive at some conclusion as to the nature of the dye used in the sample. In some cases, especially when dealing with imported colors, we may find that none of the dyes on the market are similar to the one used in the sample. It occurs quite often that manufactured goods with new dyes come to this country, before the corresponding dyes have been imported. It is necessary to have a good collection of coal-tar dyes found on the market. It is very important to keep a record of the name of the original manufacturer (in case the dyes are bought from jobbers), as very often dyestuffs of different make are different, even if they have the same trade name. The trade name should be always noted in full including different letters, B, R, G, etc., and descriptive words like "extra," "fine," etc., in order to be able to get exactly the same products should occasion occur. The record should also contain the price.

After having determined to some extent the nature of the base and coloring matter it becomes often necessary in order to confirm the findings to make a similar or even an identical sample. In this work care must be taken to use always the same grade of raw materials; it is convenient to keep on hand standard samples, of them, with names of the manufacturers, trade names, etc. One cannot make samples with chemically pure materials, as it would not be possible to duplicate them on a large scale. After a sample is made in the laboratory it is compared exactly in the same way as stated above with the tested sample. It is very important to keep a record of the yield of the color, as this will enable us to figure out the price. In computing the price from the raw materials one must always be sure to include a fair estimate for cost of labor, including also as a factor the salary of the chemist and taking into consideration the manufacturers' and jobbers' profit. In this way it is easy to tell whether the price asked for a new color is fair.

Another factor of some importance is that there is usually some little difference between a color made in the factory and one prepared in the laboratory, as it is impossible to have the conditions of work absolutely alike. It would be very wrong for a manufacturer to submit to a customer a laboratory sample for the goods that he will deliver.

The same work of preparing counter samples is often necessary in order to identify and match samples of coal-tar dyes for the use in the color trade. Two samples of dyestuffs may often stain wool or cotton in exactly the same way, but give entirely different results when used in the manufacture of colors.

After separation from the vehicle, thinners, etc., practically the same methods as those given above can be used in the examination of paints and similar goods.

BROOKLYN, NEW YORK.

THE EFFECT OF IGNITION ON THE SOLUBILITY OF SOIL PHOSPHATES.

By CHAS. B. LIPMAN

Received July 31, 1912.

In common with other soil investigators, the writer has taken occasion to point out recently the dangers involved in applying data obtained with solution cultures of plants to soil problems with the same plants. Time and again results have been obtained in solution cultures of both plants and bacteria which when compared with tests of the same organisms on soils, both sterile and unsterile, were found to be widely divergent and discordant. I have also found the same to be true regarding the purely chemical changes of the same materials in minerals and in soils as brought about by the laboratory treatment involved in their quantitative determination. My remarks apply particularly to the quantitative determinations of phosphates in soil; I employ for this paper the same title that Fraps[1] used for his recently, to call attention to the differences effected in the degree of solubility of phosphates in phosphate minerals and in soils, by ignition. In the work just cited, Fraps has shown that the ignition of phosphate minerals, including wavellite, dufrenite and variscite, for 10 minutes at a low red heat increased about 10 times the solubility of the phosphoric acid contained in them in fifth normal nitric acid and rendered it almost completely soluble in 12 per cent. hydrochloric acid. From these results he concludes that the method for determining phosphoric acid in soils as used by him is not suited to distinguish between the organic and the inorganic phosphorus in soils, since the inorganic phosphates are made more soluble through ignition.

We are not concerned in this paper with the latter conclusion of Fraps as regards the distinction between the organic and inorganic phosphorus of the soil. Having frequently noted, however, in our analytical work on soils that the very opposite effect to that above quoted is accomplished by ignition of soils before determining the phosphoric acid, it was deemed desirable to make some systematic tests with reference to the matter, and determine, if possible, the cause of the different effect of ignition on the solubility of phosphates in minerals and in soils, if such a different effect was definitely shown to exist. Accordingly five different soils were selected, each sifted through a 0.5 mm. sieve and prepared for analysis for phosphoric acid. The soils were as follows:

[1] THIS JOURNAL, **3**, 335.

No. 1. A very rich, black, fine silty loam, rich in phosphoric acid and humus, from Arroyo Grande, San Luis Obispo County, California.

No. 2. A fine sandy soil with a good supply of phosphoric acid, but poor in humus, from Escondido, San Diego County, California.

No. 3. A very heavy black, clay adobe soil with sufficient phosphoric acid for fair crop production, from West Berkeley, Alameda County, California.

No. 4. A sandy loam with a fairly good humus and phosphoric acid content from South San Francisco, California.

No. 5. A light sandy loam, of fairly good humus content and phosphoric acid, from Anaheim, Orange County, California.

The analysis was carried out as follows: Four grams of soil were placed in a porcelain cup and digested with concentrated nitric acid for two days on the steam bath. Two samples of each soil were ignited for twenty minutes at a low red heat in a platinum dish and two others of each soil were placed in the cups without ignition. The greatest caution was exercised to prevent loss by dusting in the process of ignition and in the transfer from platinum to digestion cup. After the period of digestion, the soil cups were placed on the sand bath and evaporated to dryness to dehydrate the silica, after which more acid and a little distilled water were added and the cups were replaced on the steam bath for four hours. The solutions were then carefully filtered and the soil residue washed on the filter. The filtrate was warmed to a temperature of 65° to 70° C. and the phosphoric acid precipitated with ammonium molybdate. The precipitate and solution were allowed to stand at 65° to 70° C. for about four hours, then filtered and the precipitate washed with a solution of ammonium nitrate. After this it was dissolved out with ammonia, and precipitated with magnesia mixture, then allowed to stand over night, filtered the next morning and washed with distilled water containing a little ammonia. The precipitate and filter were then dried, ignited, weighed and the phosphoric acid determined in the usual way. The percentages given represent averages of closely agreeing duplicates for each soil both ignited and unignited.

TABLE I. PERCENTAGES P_2O_5.

Soil No	1	2	3	4	5
Ignited	0.410	0.150	0.090	0.167	0.151
Not ignited	0.460	0.250	0.130	0.191	0.190

The data given in Table I leave no room for doubt as to the effect of ignition on soil phosphates as existing in various soils. In most cases the loss in percentage is not very great, but it is always definite and in some cases, as in soil No. 2, it is quite marked. In practically all cases the duplicates agreed within one hundredth of a percent. We obtain therefore the very reverse effect of ignition on the soil phosphates as existing in the soil, from that obtained by Fraps on mineral phosphates as existing in minerals. In brief, ignition of soil appears to decrease appreciably and definitely the solubility of its phosphates whether they be largely inorganic or organic. The large variety of soils employed would seem further to strengthen the evidence, in that they doubtless contained largely varying proportions of inorganic and organic phosphates and a large variety of phosphate bearing minerals.

Just why these important differences exist in the effects of ignition on phosphates in minerals and in soils is an explanation that is not as easily found as the facts which obtain in the case. It would appear to be clear that the increased solubility of the phosphoric acid in minerals like wavellite, variscite and others tested by Fraps might be accomplished through the mechanical changes induced by the heat in the mineral employed. We know for example that heating of sand will disintegrate its grains and thus produce more surface. It is altogether likely that the same happens when a phosphate mineral is ignited and the result is the production of a larger surface for the nitric acid to act upon, hence an increase in solubility of phosphoric acid in the ignited over the unignited mineral. On the other hand, in a complex material like the soil, which contains besides many kinds of mineral and rock particles in different stages of disintegration, very considerable quantities of organic matter, both decaying and in living form, and the minerals and salts in different degrees hydrated, it is probable that the mineral particles would be protected from disintegration by heat so long as the water of hydration and the organic matter still remained in the soil; therefore no additional surface would be exposed to the action of the acid and besides, the dehydration of the organic, as well as inorganic phosphates, would seem to make them less soluble. Indeed I have data to show that dehydration without ignition also decreases the solubility of the soil phosphates. This explanation is offered by the writer for the facts noted, merely as a suggestion as to the phenomena probably occurring when mineral phosphates and soils are heated, as regards their phosphate content. It is hoped that an explanation or further suggestions will be forthcoming from my colleagues. This brief paper is offered merely as a partial report on one phase of the subject of the determination of phosphoric acid in soils, the whole of which is now being studied in our laboratory. Other interesting data besides that mentioned has already been obtained which we hope to include in another paper in which the whole subject will be treated more completely.

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THE DETERMINATION OF HUMUS IN HAWAIIAN SOIL.[1]

By W. P KELLEY AND WM. MCGEORGE.

Received May 31, 1912.

In the determination of humus in soils, the difficulty of completely separating the clay from the ammonia soluble organic matter has been appreciated for some time. Certain constituents occurring in varying amounts in clays hold water of hydration which cannot be completely driven off at temperatures below the

[1] Published in detail as *Press Bulletin* No. **33**, Hawaii Experiment Station.

point of partial decomposition of the organic matter and, since humus is estimated from the loss upon incinerating the residue obtained by evaporating the ammoniacal extract, the importance of completely removing the clay is at once apparent In soils containing relatively small amounts of clay, this separation is usually a matter of comparative ease, while heavy clay soils present difficulties in varying degrees, depending largely on the specific nature of the constituents contained in the deflocculated clay. Ordinary filtration is ineffective.

A number of methods have been proposed for this determination. In some investigations in this laboratory, we have had occasion to compare some of the better known methods with soils representing a wide range both as regards mechanical composition and humus content. The soils under investigation for the most part represent heavy clays of the laterite class, such as constitute the main body of the arable lands of the Hawaiian Islands. In addition, the clay is composed of particles in a very fine state of division and possesses properties which render its separation from ammoniacal solutions extremely difficult. A few samples of highly organic soils have also been examined As will be seen from the tabular results, the humus content[1] varies from 2.64–18.27 per cent.

The type of soil, especially as regards the percentage of clay present, appears to determine in considerable measure the applicability of certain methods now in use for the determination of humus. The mechanical composition of the soils used in this investigation is therefore of some interest in this connection[2] (Table I).

Attention is called to the high content of clay and fine silt in all of these soils save Nos. 69 and 74. One of the pronounced characteristics of Hawaiian soils is a very high content of iron which exists in many cases as ferric hydrate and which imparts to the soil a red color. In connection with humus determinations it is important to know not only the proportion of clay in the soil, but also something regarding its properties, for clay is a sort of general term when applied to soils and usually has reference only to the size of the particles.

In this investigation the following methods have been used. Hilgard, Mooers-Hampton, Huston-Mac Bride or official, Cameron-Breazeale, and Rather. In all the determinations reported in this paper, except those by the Hilgard method, the solutions were made according to the official method. Since the chief obstacle to be overcome is that of removing the clay, the humus ash has been determined in each instance. By this means we were able to check the completeness of the removal of the clay. Table II shows the results as obtained by the several methods studied.

These results show a wide range of variation in the percentage of both humus and humus ash when determined by the various methods, and in addition a strict concordance is not found to exist between the results as obtained by any two methods. The results obtained by the Hilgard, Mooers-Hampton, and Cameron-Breazeale methods, it is true, are in fair agreement in certain instances, but on the whole, they are too discordant to permit of their indiscriminate use. By reference to the data for humus ash, it will be seen that none of these methods save that of Cameron-Breazeale affected a complete removal of the clay in every instance, but this method, when used in its original form, is known to bring about a loss of humus through the absorbing action of the clay filter. The Rather method in most instances brought about no coagulation of clay whatever and therefore, in its original form, is unreliable with these soils. In our use of the Mooers-Hampton method it was found to be necessary to evaporate the humus solutions to dryness in some instances as many as six times, allowing the residue to bake on the water bath for several hours and even then, upon resolution in ammonia, a partial deflocculation of the clay was unavoidable.

TABLE I. MECHANICAL ANALYSES OF SOILS USED IN EXPERIMENTS (PERCENTAGES).

SOIL NUMBERS.	69	74	97	98	99	100	101	102	103	104	108
Organic matter and combined water.	44.60	25.83	14.32	13.65	15.80	15.55	13.06	14.67	17.58	16.17	15.55
Fine gravel	5.94		0.09	0.12	0.86	0.41	0.14	0.29	0.06	0.09	0.96
Coarse sand.	26.72		0.43	0.43	0.73	1.65	0.50	0.91	0.26	0.42	
Fine sand	8.65	38.03	1.62	2.11	2.35	1.65	1.33	1.12	0.81	2.36	13.58
Silt.	4.07	16.22	3.37	3.06	9.28	6.72	6.23	7.38	5.60	6.44	6.25
Fine silt	5.09	19.99	27.19	26.32	32.69	18.45	28.88	18.87	22.70	29.07	13.35
Clay.	5.78	2.05	52.30	55.05	38.60	57.80	47.45	57.80	56.72	44.54	51.26

TABLE II. COMPARISON OF SEVERAL METHODS IN PRESENT USE. (PERCENTAGES.)

	69	74	97	98	99	100	101	102	103	104	108
SOIL NUMBERS.					Humus.						
Official method	...	...	4.30	5.94	5.12	6.38	4.64	4.34	6.31	3.54	
Hilgard method	15.63	5.26	2.43	2.61	3.68		2.95	2.71			
Mooers-Hampton method	18.74	5.32	2.68	2.70	3.17	2.32	3.72	3.20	3.72	2.68	3.84
Cameron-Breazeale method	12.30	3.98	2.34	2.38	2.91	2.24	2.85	2.24	2.94	2.36	2.29
Rather method	20.75	6.49	4.32	4.15	5.01	6.03	5.64	4.38	5.95	4.81	8.24
					Humus Ash.						
Official method			13.25	20.92	10.54	33.20	15.18	13.15	25.42	7.67	
Hilgard method	5.44	1.85	2.46	2.56	2.00		4.28	1.82			
Mooers-Hampton method	6.33	1.33	0.60	0.84	0.65	0.41	1.52	1.70	0.98	1.17	0.44
Cameron-Breazeale method	1.09	1.81	0.28	0.74	0.33	0.33	0.31	0.30	0.57	0.23	0.46
Rather method	7.71	2.51	12.94	11.43	10.40	25.69	17.61	10.28	20.49	12.74	32.69

[1] In this paper the term "humus" is used to signify the organic matter of soils soluble in 4 per cent. solution of ammonia after removing the calcium and magnesium with dilute hydrochloric acid.

[2] Analyses made by the method as outlined by Hall, "The Soil," London, 1908, Second Edition, page 51.

In the main, however, this method can be manipulated so as to remove the clay at least to a point where it is of small importance. The time required, together with the fact that the evaporation must be made in an atmosphere free from acid fumes, makes the method tedious and impracticable. From our studies on these soils and others, it appears that a partial explanation for the disagreement among the several publications dealing with the subject of humus determinations, is probably to be found in the fact that the soils studied were very different in composition and properties. With certain soils a number of these methods will no doubt give reliable results.

A MODIFIED CLAY FILTER METHOD.

From the failure to remove the clay effectively by any means other than by the use of a porous clay filter, attention was directed toward overcoming the difficulties attending its use. The essential feature of the method, as finally adopted, consists in passing a definite aliquot of the humus solution through the filter followed by dilute ammonia solution until all the organic matter is washed through, as was done by Alway, *et al.*[1]

The difficulties of this method have been overcome as follows. The solution is drawn through the filter in the opposite direction from that ordinarily employed. Instead of using the compression chamber, an ordinary suction pump was employed. The tube of glazed porcelain attached to the lower end of an 8-inch Pasteur-Chamberland filter was broken off,[2] so as to leave the end of the tube open, then the tube was inserted into the upper opening of a bell jar, such as is used for filtering under suction, in a manner similar to that employed in the use of a Gooch crucible. A large part of the tube was allowed to extend into the filtering jar and the connection made air tight (Fig. 1). It was also found desirable to coat the upper portion of the tube with paraffin, so as to prevent the passage of the solution except in the lower half of the tube. Otherwise the solution will pass down the sides of the bell jar.

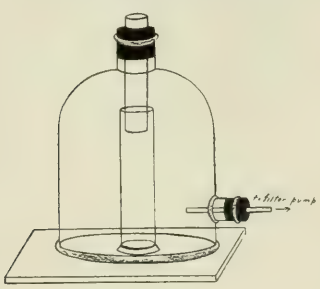

FIG. 1.

A 50 cc. aliquot of the humus solution, representing 1 gram of soil, is drawn through the tube by means of reduced pressure, the filtrate being collected in a cylinder. After this aliquot has passed through, a 4 per cent. of ammonia is then drawn through as long as it shows any color; usually about 200 cc. are required. The filtrate and washings are then evaporated to dryness and the determination completed as usual. After each filtration, the clay should be washed out of the filter tube. For this purpose, a test tube brush was found to be serviceable.

The time required to complete a filtration was found to be about $3^1/_2$ hours and by arranging a number of filtering jars in a series, an ordinary Richardson pump provided suction for at least three filters. With close fitting connections, it is probably possible to operate six filters with one pump. No attention is required other than an occasional moment for pouring in solutions and hence the filtration can be carried out along with other work without interruption. For the sake of comparison, the results obtained by the previously named methods and the modified clay filter method are submitted in Table III.

TABLE III. COMPARISON OF SEVERAL METHODS WITH THE MODIFIED CLAY FILTER METHOD (PERCENTAGES).

SOIL NUMBERS.	69	74	97	98	99	100	101	102	103	104	108
					Humus.						
Official method	...		4.30	5.94	5.12	6.38	4.64	4.34	6.31	3.54	
Hilgard method	15.63	5.26	2.43	2.61	3.68		2.95	2.71			
Mooers-Hampton method	18.74	5.32	2.68	2.70	3.17	2.32	3.72	3.20	3.72	2.68	3.84
Cameron-Breazeale method	12.30	3.98	2.34	2.38	2.91	2.24	2.85	2.24	2.94	2.36	2.29
Rather method	20.75	6.49	4.32	4.15	5.01	6.03	5.64	4.38	5.95	4.81	8.24
Modified clay filter method	18.27	5.75	2.64	2.81	3.84	3.48	3.61	3.37	4.74	3.22	3.31
					Humus Ash.						
Official method	...		13.25	20.92	10.54	33.20	15.18	13.15	25.42	7.67	
Hilgard method	5.44	1.85	2.46	2.56	2.00		4.28	1.82			
Mooers-Hampton method	6.33	1.33	0.60	0.84	0.65	0.41	1.52	1.70	0.98	1.17	0.44
Cameron-Breazeale method	1.09	1.81	0.28	0.74	0.33	0.33	0.31	0.30	0.57	0.23	0.46
Rather method	7.71	2.51	12.94	11.43	10.40	25.69	17.61	10.28	20.49	12.74	32.69
Modified clay filter method	2.14	2.19	0.54	0.75	0.57	0.64	0.78	0.70	1.12	0.76	0.99

From these data, it is obvious that the modified clay filter method gives results higher than those obtained by any other than the official and Rather methods, neither of which can be relied on with Hawaiian soils. By any of the previously used methods, it was found to be extremely difficult to obtain concordant results even with the same soil extract, while by the modified clay filter method, concordant results were easily obtained from separate extractions and in each instance the humus ash had a gray color, indicating the complete elimination of the clay.

The failure of the Rather method and other means of coagulating clay in Hawaiian soils is undoubtedly due to the peculiarities of the clay itself. Some humus solutions in which ammonium carbonate affected an incomplete coagulation of the clay were treated according to the Rather method and the coagulated and uncoagulated clay analyzed. The former appears to be made up of a mixture of ferric hydrate and

[1] Nebraska Experiment Station, *Bulletin* **115**.

[2] A Pasteur-Chamberland filter having no tubular would no doubt serve for this purpose.

silicate of aluminum, while the latter contains relatively more silica and iron and correspondingly less aluminum. In some instances it was found that a coagulation could be affected by the use of larger amounts of ammonium carbonate, while in other cases, as much as 40 grams per liter failed to produce coagulation. By the use of still larger amounts of ammonium carbonate, a partial precipitation of humus also took place.

CONTRIBUTION NO. 5, HAWAII EXPERIMENT STATION,
HONOLULU.

THE COMPOSITION OF FUSEL OIL FROM BEET MOLASSES.

By M. C. BOSWELL AND J. L. GOODERHAM.

Received May 15, 1912.

The published proximate analyses of fusel oil are very few and mostly relate to the distillates from potatoes and corn. This arises from the fact that, until comparatively recent years, fusel oil from any source was regarded as more or less valueless. In Canada, after legislation put a premium on its destruction, this product was allowed to run away in drains or used as a constituent of a cheap burning fluid. The numerous purposes to which it is now applied and for which it is indeed indispensable, have changed this custom, so that it has become four or five times as valuable as the alcohol from which it is separated.

The production of fusel oil from the fermentation of beet molasses depends industrially on a supply of crude material from beet sugar refineries, which did not come into existence on a large scale in Canada until about seven years ago. An alcohol plant, capable of handling from 30,000–40,000 tons of molasses per annum, was established in Toronto in 1905, and very considerable quantities of fusel oil have since been produced, for which a home use, or an export value, has to be found.

The researches of Ehrlich[1] carried on since 1903 ultimately led to the conclusion that the production and composition of fusel oil depend on the character of the substance fermented, mainly with relation to the quantities of leucine and isoleucine present. As beet molasses mash differs very widely from that from potatoes or grain, it might be expected that a corresponding difference would be noted in the quantities and proportions of the amyl alcohols. The particular composition of beet molasses fusel oil is hence a question of considerable technological importance.

The fusel oils of commerce differ very widely in their general characteristics, such as color, specific gravity and solubility in water, being influenced not only by the nature of the material operated on, but by the form of distilling apparatus, the process followed, and the care of the operator. The excise authorities generally look sharply after the presence of ethyl alcohol, and their requirements regarding this affect the presence of other alcohols soluble in water. In the United States, the official and commercial regulations confine the term "crude fusel oil" to that from which the lower alcohols have been so far removed by washing, that a loss of not more than 10 per cent. is realized by agitation with an equal bulk of water. The term is thus used in this paper. Hence the percentage of water-soluble alcohols in fusel oil will depend to some extent on whether the manufacturer has found it necessary to wash his oil in order to meet the excise requirements respecting ethyl alcohol.

The oil examined was amber in color. It was found that the substance or substances causing the color were soluble on shaking in dilute caustic soda. Traces of iron and copper were found, due probably to contact with these metals in the process.

The specific gravity of the sample, taken by the pycnometer, at 15° C. was 0.8370. This is somewhat higher than the figures given for fusel oil from corn, which differ widely as stated by various authorities. Worden[2] gives the range for ordinary samples of washed oil as between 0.810 and 0.835. It is evident that this character will be largely influenced by the amount of water dissolved in the oil, and also by the lower alcohols which have escaped the washing-out process.

In the fusel oil examined, the lower alcohols (ethyl, propyl and butyl) were roughly estimated by agitating equal volumes of oil and water thoroughly in a measuring tube, and noting the increase in volume of the water layer. This amounted to 8 per cent. In a similar manner the amount of water was determined approximately by agitating 10 cc. of the oil with 100 cc. of petroleum benzine and measuring the water layer. This amounted to 5 per cent. Then 500 cc. of crude unwashed fusel oil was thoroughly dried over anhydrous sodium sulphate and fractionated repeatedly until the volumes of the fractions remained constant. The result was as follows:

I.	II.	III.	IV.	V.	VI.
75°–80°	80°–85°	85°–90°	90°–105°	105°–115°	115°–120°
7 cc.	18 cc.	6.5 cc.	11 cc.	22 cc.	27 cc.

VII.	VIII.	IX.	X.	XI.
120°–125°	125°–128°	128°–130°	130°–133°	residue
29 cc.	45 cc.	260 cc.	33 cc.	10 cc.

TOTAL, 473.5 cc. WATER, 20.0 cc. LOSS, 6.5 cc.

A sample of the crude oil was thoroughly agitated with water, and the oil separated and dried: 500 cc. of this on fractionation gave the following:

I.	II.	III.	IV.	V.	VI.
75° 80°	80°–85°	85°–90°	90°–110°	110°–115°	115°–120°
none	none	very little	10 cc.	10 cc.	25 cc.

VII.	VIII.	IX.	X.	XI.
120°–125°	125°–128°	128°–130°	130°–133°	residue
40 cc.	75 cc.	278 cc.	51 cc.	10 cc.

TOTAL, 499 cc. LOSS 1, cc.

On comparing the results of the two fractionations it will be noted that fractions I, II and III have practically disappeared from the washed oil. These were identified, as will be shown later, as lower alcohols which are more or less soluble in water.

Although the boiling points indicated the particular alcohols which were present in the various fractions it was decided to substantiate this by transforming the alcohols into esters. On examining the literature, it was found that the esters of acetic acid were more completely described than those of any other acid, and consequently served best for purposes of identification. Action with acetyl chloride alone was found

[1] Summarized in Harden's "Alcoholic Fermentation," **1911**, 75–82.

[2] Worden, *Nitro-cellulose Industry*, **1**, 208.

to be unsatisfactory, yielding a mixture in each case difficult to fractionate, and always leaving a high boiling residue, indicating that the reaction was not one of simple esterification alone.

The method of Einhorn[1] was adopted and proved very satisfactory.

Accordingly 10 grams of each fraction were dissolved in about 60 grams of pyridine, and a little more than the theoretical quantity of acetyl chloride was added. After standing for 6–8 hours the mixture was poured into cold dilute sulphuric acid. The ester which separated as an oil was dried over anhydrous sodium sulphate and fractionated.

The following were the results:

Fraction I (75° 80°).—See table.—The boiling point indicated ethyl alcohol, which was confirmed by the iodoform reaction.

Fraction II (80°–85°).—The b. p. indicated the presence of isopropyl alcohol—b. p. 82.8°. The ester on fractionation boiled chiefly at 90°–94°, the boiling point of isopropyl acetate. This fraction was hence largely isopropyl alcohol.

The boiling points of fractions III and IV, as well as fractions VII and VIII made it difficult alone to decide with certainty as to the particular alcohols present. However, upon transformation into acetic esters, and careful fractionation, it was found possible to identify them.

Fraction III (85°–90°).—As this fraction was very small, it was esterified and added to the ester from fraction IV.

Fraction IV (90°–105°).—The ester distilled chiefly between 110°–120°. It was hence the isobutyl ester—b. p. 115–°117°. A little isopropyl, and traces of amyl esters, were also detected.

Fraction V (105° 115°).—The b. p. indicated the presence of isobutyl alcohol—b. p. 108°. The largest portion of the ester was recovered at 110°–120°, the temperature being very constant at 115°–117°, indicating isobutyl ester. A very small quantity of normal butyl ester, with a boiling point of 125°, was obtained. This fraction hence consisted chiefly of isobutyl alcohol with some normal butyl alcohol.

Fraction VI (115°–120°).—The b. p. indicated the presence of normal butyl alcohol—b. p. 117°. The main portion of the ester came over at 120° to 130°; mostly at 125°, the boiling point of the n. butyl ester. Some methyl normal propyl carbinol ester, with a boiling point of 133°–135°, was recovered also. This fraction hence consisted chiefly of *n.* butyl alcohol with some methyl normal propyl carbinol.

Fraction VII (120°–125°).—The ester of this fraction on distillation separated very sharply into two fractions, the larger with b. p. 133°–136° indicating methyl normal propyl carbinol ester, and the smaller with b. p. 138°–139° indicating isoamyl ester. Hence, this fraction consisted chiefly of methyl *n.* propyl carbinol with some isoamyl alcohol.

Fraction VIII (125°–128°).—A small portion of ester came over between 130° and 137°, containing some methyl *n.* propyl carbinol ester. The largest fraction, which was very constant, distilling between 137–140°, represented the isoamyl ester. This fraction was chiefly isoamyl alcohol, with a little methyl *n.* propyl carbinol.

Fraction IX (128°–130°).—The b. p. indicated the presence of active amyl alcohol, b. p. 128.5°. Practically all the ester came over between 141° and 142°, being the boiling point of active amyl ester, with a small amount of the isoamyl ester, which boils at 137°–140°. This fraction was hence chiefly active amyl alcohol, with a small amount of isoamyl alcohol.

Fraction X (130°–133°).—The b. p. indicated the presence of isoamyl alcohol, b. p. 131.5°. Practically all the ester came over between 138°–140°, proving it to be the isoamyl ester, with a small quantity of active amyl ester. This fraction hence consisted of isoamyl alcohol with some active amyl alcohol.

The Residue (XI), which amounted to 10 cc., was placed in a small flask and distilled. About 8 cc. came over below 150°; a very little up to 180°; and about 1½ cc. was left in the flask. This last residue appeared to have decomposed with the production of brownish vapor. The 8 cc. that came over was esterified and the ester fractionated, and found for the greater part, to distil between 135° 140°, being the boiling point of the isoamyl ester. That which was collected at 140° 150°, and was fairly constant between 141° 142°, was the active amyl ester. Very little came over above 150°, but if a sufficient quantity had been available, would probably have been found to consist of the hexyl and heptyl esters. This residue hence consisted of isoamyl alcohol and active amyl alcohol, with probably small quantities of higher alcohols.

There were no semi-solid substances observed toward the end of the operation as has sometimes been the case with fusel oil from corn.

Ten grams of fusel oil were titrated against a standard potash solution using phenolphthalein as the indicator. 100 grams of fusel oil contained 4.5 cc. normal acid. This is equivalent to 0.5 per cent. free acid in the oil, calculated on C_5H_{11}—COOH as a basis.

Ten grams of fusel oil were boiled with 75 cc. of 0.5 N.KOH for one hour, under a reflux condenser. After cooling, the excess of alkali was titrated against standard acid.

One hundred grams of oil contained 18.4 cc. of normal free acid and acid from esters. Of this quantity, 4.5 cc. were free fatty acids, while the balance (13.9 cc.) represented the acids from the esters. Using $C_5H_{11}COOC_5H_{11}$, the amyl ester of capronic acid, as a basis for calculation, this is equivalent to 2.5 per cent. ester in the oil.

The bases present in the oil were separated in the usual manner. The amount was too small for purification and estimation. However, the distinctive odor of pyridine was recognized.

Furfurol could not be detected.

Consequently, "the composition of fusel oil from beet molasses" may be summarized as follows:

		Cc. from 500 cc.	Per cent.
Ethyl alcohol		5	1
Isopropyl alcohol		20	4
Isobutyl alcohol		30	6
n Butyl alcohol		30	6
Amyl alcohols	Methyl *n.* propyl carbinol	40	8
	Active amyl alcohol	210	42
	Isoamyl alcohol	130	26
Fatty acids		2.5	0.5
Esters of the fatty acids		12.3	2.46
Pyridine and other bases		Present	Present
Hexyl alcohols, etc.		Traces	Traces
		479.8	95.96
Water		20.0	4.00
Total		499.8	99.96

This composition does not present any marked difference of practical importance from that given for corn by LeBel,[1] and largely quoted, which is as follows:

	Per cent.
Normal propyl alcohol	3.69
Isobutyl alcohol	15.76
Amyl alcohols	75.85
Hexyl alcohols	0.13
Free fatty acids	0.16
Fatty acid esters	0.30
Terpines and terpine hydrates	0.08
Furfurol, heptyl alcohol and bases	0.02
	95.99

[1] Liebig's *Annalen*, **301**, 95 (Einhorn).

[1] Maercker's "Spiritusfabrication," p. 83.

The amount of total amyl alcohols, which, industrially, is the chief point, shows a difference of only 0.15 per cent. The respective figures for butyl alcohols differ by 3.76 per cent., though the propyl closely corresponds. This is, however, of little importance, as it shows only that one sample of oil was washed more than the other.

TORONTO, CANADA.

DIFFICULTIES IN THE COLORIMETRIC ESTIMATION OF VANILLIN.[1]

By W. S. HUBBARD.

Received July 19, 1912.

Moerk,[2] in 1891, found in testing for vanillin that he had some difficulty in always obtaining the ferric chloride color reaction, and tried using a ferrous salt and oxidizing it with bromine water. In the latter case, he found the color much more intense than with ferric chloride and was able to detect 1 : 100,000 instead of 1 : 2,000 as before. In a paper[3] a month later he proposed a colorimetric estimation of vanillin in vanilla extracts by this means and his method with a few modifications was later adopted by the Bureau of Chemistry.[4] The procedure is as follows:

"Measure 2 cc. of the vanilla extract into a test tube and add about 5 cc. of lead hydrate; mix thoroughly, pour upon a small wet filter, collect filtrate and washings in a 50 cc. graduated Nessler tube; add an excess of bromine water (3 or 4 drops) and sufficient freshly prepared 10 per cent. ferrous sulphate solution to produce the maximum bluish-green color that will result if vanillin is present, and fill to the mark with water."

"Compare with solutions containing a known amount of vanillin treated as directed above." The lead hydrate is prepared as follows:

"Dissolve 200 grams of lead acetate in 850 cc. of water, filter and add an excess of potassium hydroxide. Let the precipitate settle and wash thoroughly by decantation with repeated portions of water until perfectly neutral. Keep in 500 cc of water in the reagent bottle, and shake to form an emulsion-like mixture before adding to decolorize."

The above method has been used in this laboratory with indifferent success for the past two years. Not until this year were the standards put through the treatment with lead hydrate as is directed in the method: then the troubles quickly multiplied. It was noticed that it was not always possible to match two standards containing the same amount of vanillin and treated in a like manner. An attempt was made to locate the trouble by means of a number of experiments.

Four cc. each of three solutions of vanillin standard made up according to the directions given in Bulletin 107, but containing 0.05, 0.10 and 0.20 gram of vanillin per 100 cc. respectively, were treated with lead cream, centrifuged and filtered, ferrous sulphate and bromine added, and diluted to 50 cc. with water. No difference in color could be noticed among the three and they showed about $^1/_8$ the color of a sample of four cc. of the 0.05 gram in 100 cc. sol. not treated with lead cream. Inasmuch as lead sulphate was precipitated out when the ferrous sulphate and bromine were added it was thought possible that this precipitate mechanically carried down some vanillin.

Since vanilla contains small amounts of oxalic acid and phosphates, 4 cc. of vanillin standard (0.05 in 100) was treated with 5 drops of 85 per cent. phosphoric acid and then with lead cream. It was not necessary to centrifuge as the lead agglutinated immediately, and on the addition of the ferrous sulphate and bromine water no precipitate was formed. The solution matched up to a standard untreated with lead except that it was of a purplish color. But if four drops of phosphoric acid were used instead of five, a precipitate was formed on the addition of bromine water and ferrous sulphate and the color did not match an untreated standard.

A series of experiments were carried on in the same manner with malic acid instead of phosphoric, and it was found that 0.5 cc. of a 10 per cent malic acid gave the best results; the solution had the characteristic bluish green color instead of being purplish as with the phosphoric acid. On standing four weeks, the samples acquired a yellowish tinge in comparison to freshly prepared samples.

In the original method of Moerk[1] a few drops of ferrous sulphate are added and then the bromine drop by drop to a maximum color. In the method of the government, however, an excess of bromine is added and sufficient ferrous sulphate to produce the maximum color. A number of experiments were carried out to see if it made any difference which way it was done and to find the limit in amount of ferrous sulphate and bromine water if any. One cc. of standard vanillin solution (0.05 in 100) was used in all cases.

TABLE I.

Experiment Number.	1.	2.	3.	4.	5.	6.	7.	8.
Drops $FeSO_4$ sol.	1	2	3	4	5	6	7	8
Drops Br sol.	2	2	2	2	2	2	2	2
	Of equal intensity					Lighter but equal		
One more drop Br sol	Increases intensity					Intensity same as 3, 4 & 5		
One more drop Br sol.						Intensity same as 3, 4 & 5		

TABLE II.

Experiment Number.	9	10	11	12	13	14	15	16
Drops $FeSO_4$ sol.	8	9	10	11	12	13	14	15
Drops Br sol.	4	4	4	4	4	4	4	4
	Of equal intensity				Of equal intensity			
One additional drop Br sol.	All of equal intensity							

TABLE III.

Experiment Number.	17	18	19	20	21	22	23	24
Drops Br sol	5	5	5	5	5	5	5	5
Drops $FeSO_4$ sol.	1	2	3	4	5	6	7	8
	No color	Darkest and equal					Lighter and equal	

It was found that after obtaining the maximum color in the above tests and then diluting to 50 cc. with water, it was necessary in every case to add at least 2 drops more bromine water to bring the color up to a maximum, and this could not be accomplished by adding the extra

[1] Read at the February meeting of University of Michigan Section of the A. C. S. I wish to thank Dean J. O. Schlotterbeck for his interest in my work.

[2] *Am. J. Pharm.*, **63,** 521.

[3] *Ibid.*, 572.

[4] *Bull.* **107,** (revised) p. 157.

[1] *Am. J. Pharm.*, **63,** 521.

2 drops of bromine water before diluting. When the bromine water was added first and the color developed with ferrous sulphate and diluted, a deeper color could not be obtained by the addition of more bromine water (Table III). It was noted too that those which had a larger proportion of ferrous sulphate gave the deeper color, a fact also noted by Flückiger and Nagelwort.[1] In those in which the bromine was added first (Table III) the color was not nearly as deep as in those in which ferrous sulphate was added first (Table I). It was found that it took 2.5 cc. of the vanillin solution (0.05 in 100) when bromine water was added first, to equal 1 cc. when ferrous sulphate was added first.

One cc. of pyrocatechuic acid (equivalent to the one cc. of vanillin) and 2 drops of ferric chloride added gave the same depth of color as 1 cc. of vanillin when treated with ferrous sulphate and bromine water.

Carles[2] in 1872 and Tiemann[3] and Haarmann in 1874 showed that a water solution of vanillin gave a precipitate, soluble in hot water, with a concentrated solution of lead acetate. The lead salt has the formula $(C_8H_7O_3)_2Pb$. In trying lead acetate and also lead nitrate solutions we were unable to get any precipitate with a water solution of vanillin of the strength usually met with in extracts. When, however, the clear, neutral filtrate from lead cream was added to the vanillin solution there appeared immediately a yellow precipitate. This precipitate when dissolved gives the color with ferrous sulphate and bromine water. Some of the yellowish precipitate was extracted with ether and the ether evaporated, leaving a crystalline mass which responded to the vanillin color reaction. On standing 12–24 hours, colorless, rosette like crystals formed in the filtrate from which the yellow precipitate was filtered out. The crystals were soluble in hot water and when massed together in some quantity had a yellow color similar to the first precipitate.

A number of analyses were made of the precipitate which comes down immediately and were as follows: The precipitate was dissolved in a little dilute acetic acid and hydrogen sulphide passed in, the lead sulphide washed, dried and weighed as such.

RESULTS.

	Wt. of lead vanillin. Gram.	Wt. of PbS. Gram.	$Pb(C_8H_7O_3)_2$. Pb.
Theoretical.	0.357		1.724
A	0.09695	0.0626	1.771
B	0.1238	0.0858	1.666
C	0.0946	0.0732	1.48
D	0.1130	0.0864	1.50
E	..	..	..
F	0.0642	0.0370	1.98
		Average,	1.687

The filtrate from the lead showed a strong color reaction for vanillin.

CONCLUSION.

In the official colorimetric estimation of vanillin in vanilla extracts, it is difficult to get a maximum color.

The original method of adding the ferrous sulphate first gives a deeper color than that of the present method when the bromine is added first.

In a vanilla extract it is very difficult to add only enough lead cream to decolorize the solution and when different amounts of lead cream are used different depths of color are obtained.

Dilution of the sample influences the color.

It is shown that much larger amounts of ferrous sulphate are necessary in comparison with bromine water to produce a maximum color.

It is shown that the lead cream forms a lead vanillin compound of the formula $(C_8H_7O_3)_2Pb$ and such being the case a quantitative estimation is impossible where lead is used.

It seems quite likely that the vanillin is oxidized to pyrocatechuic acid.

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[1] "Reactions," p. 152, by Flückiger.
[2] *Bull. soc. chim.*, **17**, 2
[3] *Ber. Chem. Ges.*, **7**, 614.

A NEW COLORIMETRIC METHOD FOR THE DETERMINATION OF VANILLIN IN FLAVORING EXTRACTS.

By OTTO FOLIN AND W. DENIS.

Received July 1, 1912.

As the Hess-Prescott method for the determination of vanillin, which in the modified form proposed by Winton and his associates[1] is now universally used in American food laboratories, is extremely laborious, although undoubtedly accurate, it has seemed worth while to attempt to work out a rapid colorimetric method for use in this determination.

The time spent at present by the food analyst on the quantitative determination of vanillin in flavoring extracts is out of all proportion to the value of the results when judged by the weight given them in passing judgment on the quality of commercial extracts.

By the use of the phosphotungstic-phosphomolybdic reagent recently described[2] we have been able to work out a colorimetric method for the determination of vanillin which gives theoretical results with purely artificial extracts containing known amounts of the substance, and gives with authentic extracts values agreeing closely with those obtained by the official method.

Solutions Required.—(1) An aqueous solution of pure vanillin to be used as a standard. This should be made of such a strength that 10 cc. contains one mg. of vanillin.

(2) The phosphotungstic-phosphomolybdic acid reagent, prepared as follows: To 100 grams pure sodium tungstate and 20 grams phosphomolybdic acid (free from nitrates and ammonium salts) add 100 grams syrupy phosphoric acid (containing 85 per cent. H_3PO_4) and 700 cc. water; boil over a free flame for one and a half to two hours; then cool, filter if necessary, and make up with water to a volume of 1 liter An equivalent amount of pure molybdic acid may be substituted for the phosphomolybdic acid.

(3) A solution of pure sodium carbonate saturated at room temperature.

[1] *J. Am. Chem. Soc.*, **21**, 256 (1899); **24**, 1128 (1902); **27**, 719 (1905).
[2] *J. Biol. Chem.*, **12**, 239 (1912).

(4) A solution containing 5 per cent. basic and 5 per cent. neutral lead acetate.

Vanillin (and also other mono-, di-, and tri-hydric phenol compounds) when treated in acid solution with the phosphotungstic-phosphomolybdic reagent above described gives on the addition of an excess of sodium carbonate a beautiful deep blue color admirably suited for quantitative colorimetric work.

At first an attempt was made to prepare the color directly from the untreated extract it was found, however, that this gave too high results, due probably to the fact that the tannin and tannic acid present in all true vanilla extracts also react with the reagent.

The following procedure has therefore been devised and has given admirable results with a long series of extracts: 5 cc. of the vanilla extract to be examined are transferred by means of a pipette to a 100 cc. volumetric flask and about 75 cc. cold tap water are added: 4 cc. of the lead acetate solution are then poured in and the mixture made up to volume with water.

The contents of the flask are then rapidly filtered through a folded filter paper, and 5 cc. of the filtrate are transferred by means of a pipette to a 50 cc. volumetric flask. In another 50 cc. volumetric flask is placed 5 cc. of the standard vanillin solution; then 5 cc. of the phosphotungstic-phosphomolybdic reagent is added to each flask, the reagent being allowed to run down the neck of the flasks in order that any vanillin adhering thereto may be washed down. After shaking, the flasks are allowed to stand for five minutes and are then filled to the mark with saturated sodium carbonate solution. After inverting the flasks two or three times, in order that the contents may become thoroughly mixed, they are allowed to stand for 10 minutes, by wihch time the precipitation of sodium phosphate is complete. The contents of the flasks are then rapidly filtered through a folded filter paper and the color of the resulting clear deep blue solutions compared by means of a Dubosc colorimeter. The standard solution is best placed at 20 mm. as experiment has shown that the color produced by the amount of vanillin contained therein (1 mg. in 100 cc.) is most accurately and easily read at this point.

In this, as in all other colorimetric methods, a slight cloudiness of the solution to be read, by cutting off more light than the standard, gives a reading much too low, with correspondingly high results; consequently no solution should be read which is not absolutely clear after filtration.

The calculation of the results is not complicated. When 5 cc. of the solution (previously diluted 5 : 100) is taken, this corresponds to 0.25 cc. of the original solution. If 10 cc. are taken they correspond to 0.5 cc. of the original. Since 0.5 mg. vanillin is used as a standard and with the standard set at 20 (mm.), $0.5 \times 20/R = X$ where R is the colorimeter reading of the unknown and X is the amount of vanillin in mgs. present in the volume of the original extract used in the final color comparison: 100 X divided by the volume of extract taken expressed in mgs. gives the result in per cent.

For example, if 5 cc. of the diluted and filtered solution gave a reading of 18 mm. the result would be $0.5 \times 20 \div 18 = 0.555$ mg.; $55.5 \div 250 = 0.22$. Hence 0.22 per cent. vanillin.

As outlined above, an analyst familiar with the method can in one hour easily make vanillin determinations in from ten to twelve samples of vanilla extract.

Another point in favor of the new method is that by its use the amount of material needed for a vanillin determination is reduced to a minimum, 2.5 cc. of extract being sufficient for from two to four duplicate determinations.

Besides the direct determination of vanillin, the colorimetric method may also be used as a check on the official method.

After the vanillin has been extracted with ether, dried to constant weight, etc., in the usual way, a more or less white crystalline substance is obtained which is usually considered pure vanillin; it is possible by the colorimetric method for the analyst to obtain a check on his results which will at once indicate to him whether the substance extracted and weighed is pure.

This determination is best made as follows:

Dissolve the residue in the dish in the smallest possible quantity of 25 per cent. ethyl alcohol, transfer to a volumetric flask and make up with water to such a concentration that 10 cc. of the solution shall contain 1 mg. of the residue. To 5 cc. of this solution add 5 cc. of the phosphotungstic-phosphomolybdic reagent, as described above, and compare with a similarly treated standard.

For successful use of the above method the following precautions should be noted;

Before beginning a series of determinations the standard solution should be placed in both cups of the colorimeter and the operator should satisfy himself that with the available light he can read the standard to within at least 0.2 mm. We have found that satisfactory readings can be made at night by the use of an ordinary incandescent electric light, the bulb of which is covered by a sheet of white paper. It becomes even more important, however, when artificial light is used, that the standard solution be placed in both sides of the colorimeter, both prisms set at 20 mm. and the instrument moved about until equal illumination of both fields is secured.

We have satisfied ourselves by numerous experiments that it is possible by this method to read against each other solutions containing widely varying amounts of vanillin (as for example, a solution containing 1 mg. vanillin in 100 cc. against one containing 0.5 mg. vanillin in the same vessel); as, however, in all colorimetric work it is a recognized fact that accuracy of reading is increased when the concentration of standard and unknown are not too widely divergent, it is suggested that with the standard at 20 mm. no reading of the unknown be accepted as final if the reading fall much above 15 mm. or below 30 mm. Should the reading obtained fall outside these limits a greater or less amount of the filtrate from the lead precipitate should be taken and the determination repeated.

A new portion of the standard must be prepared

for each batch of readings made, as the color darkens slowly for about an hour after the addition of the alkali.

It will usually be found that twelve samples constitute the maximum number that can be satisfactorily manipulated at one time.

VANILLA EXTRACTS MADE IN THE LABORATORY ACCORDING TO THE SPECIFICATIONS OF THE U. S. PHARMACOPOEIA

Laboratory number	Kind and quality of beans from which prepared	Per cent vanillin by Official method.	Per cent vanillin by Colorimetric method.
1	Mexican first	0.17	0.17
3	Mexican second	0.17	0.16
6	Mexican third	0.19	0.19
10	Mexican fourth	0.19	0.19
11	Mexican fifth	0.15	0.15
14	Bourbon first	0.20	0.20
17	Bourbon second	0.15	0.16
21	Bourbon third	0.20	0.21
24	Bourbon fourth	0.15	0.16
29	Bourbon fifth	0.16	0.16
30	Seychelles first	0.19	0.20
33	Seychelles third	0.21	0.21
37	Seychelles fourth	0.18	0.18
39	Madagascar second	0.23	0.21
42	Madagascar third	0.21	0.20
47	Madagascar fourth	0.24	0.24
48	Comores first	0.19	0.19
51	Comores third	0.19	0.19
54	Comores fourth	0.12	0.13
59	Comores second	0.25	0.24
64	South American first	0.23	0.25
65	South American second	0.19	0.19
66	South American splits	0.22	0.22
	Java fourth	0.23	0.22
	Tahiti	0.11	0.10
	Vanillons	0.06	0.07

Through the kindness of Dr. A. L. Winton we have been able to secure a large number of authentic vanilla extracts which were prepared from various grades of beans in the U. S. Food and Drug Inspection Laboratory at Chicago. Dr. Winton has also allowed us to use as a control on our new method the vanillin figures obtained in his laboratory on these extracts by means of the official method.[1]

Through the kindness of Mr. B. H. Smith, of the Boston Laboratory, and of Mr. R. S. Hiltner, of the Denver Laboratory of the U. S. Food and Drug Inspection Service, we have also been able to secure samples of the vanilla extracts sent out for coöperative work in 1911 by the referee on flavoring extracts of the association of official agricultural chemists. Mr. Hiltner has also sent us the average vanillin figures obtained by the official method on these extracts by the chemists coöperating with him. In all somewhat more than a hundred samples of vanilla extract have been assayed for vanillin by our colorimetric method and in no case has there been any marked deviation from the values obtained by the official method.

Above are given a number of examples of the values obtained by the colorimetric method. These represent but a fraction of the number of results obtained, but the figures agree so uniformly with those given by the official method that it seemed useless to take up more space in this connection.

Below are given results obtained with a few miscellaneous extracts; again the vanillin figures reported as obtained by the official method were furnished us in part by Dr. Winton and in part by Mr. Hiltner.

No.	Prepared from:	Percentage vanillin by Official method.	Percentage vanillin by Colorimetric method
I	Mexican beans, 60% alcohol and glycerine.	0.20	0.20
II	Bourbon beans, 60% alcohol and sugar (U. S. P.)	0.19	0.19
III[1]	Mexican and Tahiti beans and maple syrup, prune juice, synthetic vanillin and caramel	0.18	0.17
IV[2]	25% tonka extract, 75% prune juice, 0.15% vanillin and caramel coloring	0.15	0.16

[1] A. U. S. P. extract.

[2] An entirely artificial extract.

It is a well known fact that vanillin even in fairly dilute solution may be precipitated by basic lead acetate. We have satisfied ourselves, however, that in the very high dilutions employed in our method no vanillin is precipitated by the lead.

Coumarin, extract of tonka bean and acetanilid give no color with the phosphotungstic-phosphomolybdic acid reagent; the presence of sugar, caramel, or glycerine does not in any way interfere with or alter the color formation.

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METHOD FOR DETERMINING FAT IN SUGARED EVAPORATED MILK.

By F. C. BROEMAN.

Received June 8, 1912.

Ten grams of the milk are mixed with 100 cc. of hot water and 5 cc. $CuSO_4$ solution (Feh. St.) added and stirred. The ppt. contains the fat and it is filtered at once and washed with hot water. It is then transferred to a 150 cc. beaker (after a little experience it can be thrown out without a particle sticking to the paper) and 10 cc. conc. HCl added. Heat on hot plate until solution turns to chocolate brown, cool and then add 2–3 times volume of alcohol and extract 4 times with petroleum ether in separatory funnel. The results obtained agree with those obtained by the extraction methods when carried out under the most exacting conditions. The determination can be completed entirely in one hour.

LABORATORIES OF F. C. BROEMAN & CO.,
CINCINNATI, OHIO.

LABORATORY AND PLANT

A NEW TYPE OF INORGANIC FILTER FOR LABORATORY PURPOSES.

By M. A. WILLIAMSON AND P. A. BOECK.

Received July 15, 1912.

The use of porous inorganic materials for filtration and separation of liquids and solids in quantitative work has been known for some time. A variety of materials and shapes have been employed for this purpose with more or less success.[1]

[1] *Bull.* **107**, 156 (Revised), Bur. of Chem.

[1] See Faraday's "Chemical Manipulation," new edition, 1830, Section 9, page 230, and *J. Am. Chem. Soc.*, **9**, 22, article by Lucius Pitkins on the "Efficiency of Porcelain Filters.

The work encountered in analytical operations is so varied in character and is subject to such extremely severe conditions, that most of the materials tried have been found lacking in some one or more desirable characteristics, such as resistance to the influence of the re-agents employed, with the results that their successful application to quantitative work has been seriously curtailed.[1]

There are two general methods of using porous inorganic filters.

1. A finely divided material which is placed loosely on a perforated or porous body, permitting the passage of the liquids, the solid matter being retained by the finer voids in the filtering medium.[2] Well known examples of this class of filter which are used for quantitative analytical work are sand, glass, wool, kaolin, clay, precipitated alumina, natural porous stones and infusorial earths, which may be used either with or without an organic material.

2. Bonding together these finely divided materials by means of some agglutinant which is insoluble in the solutions filtered and which does not occupy all the space between the grains or voids in the body. A massive but porous filtering bed is obtained which may be made into a variety of shapes whose filtering capacity can be varied by altering the size and number of the voids. This can be accomplished in several ways; by varying

1st, the relative sizes of the particles bonded;

2nd, the proportion of the various sizes of grain used;

3rd, the percentage of bonding material used;

4th, the shrinkage of the bonding material;

5th, the addition of some material which can be subsequently removed by ignition or solution, leaving the volume occupied by it as a void.[3]

For analytical work the use of a porous diaphragm or shape offers so many advantages that it has been the subject of much speculation and a variety of materials have been tried out. The advantage is strongly in favor of the bonded articles, as they are immediately available without previous preparation. The asbestos fiber Gooch crucible and Witte plate are good examples of the first class of these materials, but with the exception of soluble precipitates it has the disadvantage of requiring frequent renewal and preparation.

In carrying out the investigation on refractory aluminous bodies for high temperature work it was found that bodies made up of fused alumina, bonded with a highly resistant bonding material of porcelain nature, were very advantageous.

Tests conducted on the fused alumina alone showed it to withstand the action of both acids and alkalis in solution, quantitatively. Similar tests on the bonding material alone indicated that it was affected by only the strongest acids and alkalis and even then to so small an extent that with the proper precautions it could be used for quantitative chemical operations in practically any solution.

[1] See *J. Am. Chem. Soc.*, **3 4**, 248, article by P. Casamajor. Also *Chem. News*, **32**, 45, article P. Casamajor, on "Implements of Filtration."

[2] See *J. Am. Chem. Soc.*, **8**, 192, article by J. H. Stebbins, Jr. "The Micromembrane Filter." Also *J. Am. Chem. Soc.*, **27**, by Mr. Porter W. Shimer on a "New Filter."

[3] Article appearing in the German Chemical Society, sixth year, No. 8, page 227, by W. Pukall. "Treatise on Clay Filters, their Properties and Application in Chemical and Bacteriological Laboratories."

MANUFACTURE OF CRUDE MATERIAL AND PROPERTIES OF FINISHED PRODUCT.

The fused alumina, the material used in the manufacture of the filters to be described, has been used for the past ten years in the manufacture of abrasive wheels and stones under the trade name of "Alundum." It is obtained by fusing calcined hydrated oxide of alumina or bauxite in a water cooled electric arc furnace, from which it comes in the form of an ingot weighing some three tons. The impurities contained in the bauxite as iron oxide, silica, and titanium oxide are reduced to a certain extent and segregated at the bottom of the pig as a low grade ferro-silicon containing some titanium. The resulting pig or ingot consists essentially of pure crystalline alumina. The physical properties of this material adapt it peculiarly well to the manufacture of refractory laboratory articles. On being crushed, it is graded to a uniform mesh and mixed with the required amount of bonding material, the character of which is determined by the uses to which the resulting article is to be put. When made into the form of bonded shapes these materials have been found to possess a high thermal coefficient. The following curves illustrate graphically the relative thermal conductivity of ordinary fire-brick, Seger porcelain, bonded Alundum and bonded Crystolon at comparatively low temperatures. The finished articles also possess an extremely

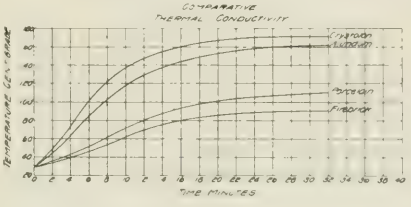

FIG. 1.

high melting point, approximately 1900° Centigrade, or 3500° Fahrenheit, a comparatively low coefficient of expansion 0.0000071 per degree C., and are non-conductors of electricity. This dielectric property was determined by Dr. Thompson, of the Massachusetts Institute of Technology, and is found to be greater than that of porcelain, even at high temperatures. The specific resistance of centimeter cubes at various temperatures are as follows:

Degrees C.	Megohms
528	130
720	16
892	5.3
1020	1.8

The maximum crushing strength of bonded Alundum is 15,410 lbs. or $7^1/_2$ tons per square inch while its tensile strength is 1,700 lbs. per square inch. This factor is dependent on the thermal conductivity, coefficient of expansion and other properties desired.

These articles have furthermore been found remarkably resistant to the action of fluxes, especially those of a basic nature even at high temperatures,

GENERAL REQUIREMENTS OF LABORATORY FILTERS.

The general requirements of a filter for laboratory work are, sufficient porosity permitting them to be used for a variety of purposes, rapid cleansing and preparation for subsequent operations. They should possess sufficient strength to resist a high degree of suction and withstand the moderately high temperatures encountered in the ordinary laboratory for igniting the filter; inactivity towards reagents and materials which are ignited in them; constancy in weight within the practical limits of error through ordinary quantitative treatment.

In the platinum Gooch all of these desirable properties are found. It, however, possesses the disadvantage of requiring careful preliminary preparation of the asbestos mat. The cost of platinum, unfortunately, places it beyond the reach of the every-day analyst, also the precautions to be exercised in the use of this ware handicap the operation.

With porcelain, several difficulties are encountered: (1) the time and trouble necessary in preparing the asbestos mat and in varying the thickness in order that any desired degree of porosity may be obtained; (2) the comparatively low thermal conductivity of porcelain is a militating factor in several ways, as in the ashing of organic compounds, burning off precipitates, etc., increasing the time appreciably. Porcelain can be used at only relatively low temperatures in comparison with this new material.

The articles made from fused alumina or Alundum will be found to possess most of the desired advantages. They are rapid, always ready, easily cleansed, withstand any temperatures available in the average laboratory; the porosity can be varied to meet any requirement; they will withstand the action of practically all reagents and materials ignited in them. They are not adapted to making fusions with alkaline carbonates or similar material, because of the siliceous nature of the bond. Like porcelain they are fragile, and will withstand but moderately sudden temperature changes. On the other hand, however, they possess a high thermal conductivity which together with the porosity makes them better adapted than porcelain to the burning off of organic materials.

OBJECTIONS TO ALUNDUM.

One disadvantage in making filtrations with the ordinary shaped crucibles of fused alumina was found in that they were not placed in the carbon tube far enough to bring the entire filtering area into the zone of suction. The portion which projected beyond the zone of suction became impregnated with the soluble salts in the solution being filtered which could only be removed after prolonged washing, consuming so much time that in many operations this crucible did not offer any particular advantages over the Gooch. Several methods were developed, employed and found excellent, only they required more time and apparatus than the ordinary porcelain Gooch.

To overcome the foregoing objection, glazing the upper portion of the crucible was attempted. The idea was to obtain a crucible of fused alumina with impervious walls and a porous bottom. This promised a solution of the difficulty in analytical work, but owing to the fact that the walls were impervious to all glazes, it was found that the glaze simply spread over the surface, leaving a porous strata of Alundum between the walls of glaze. This is an extremely unsatisfactory condition in filtering off any precipitate. The porous strata would become impregnated with a solution containing salts impossible of removal, causing an increased weight in the crucible and the possibility of contaminating any solution which would be passed through it afterwards.

The idea of building up crucibles of two parts, that is, glazing the upper portion and cementing it to a porous bottom, was tried out, but found subject to the same objections. Accordingly this scheme had to be abandoned.

Another difficulty experienced by some is the property of Alundum to absorb moisture from the air. This is by no means a chemical action for there is nothing in the bond or the fused alumina which will combine with water at ordinary temperatures. The moisture of the air is simply condensed on the walls of the voids or pores, which action can continue only up to the point of saturation; that is, when a crucible of this material is ignited and immediately weighed it will be found to gain in weight when exposed to the air. Upon again igniting, it will return to the former weight. This variation, however, is so limited that in ordinary determinations it becomes a negligible quantity. The action can be observed more plainly by reference to Table I. Four Alundum crucibles (marked 1, 2, 3 and 4), one 30 cc. porcelain Gooch

TABLE I.—ABSORPTION PROPERTIES OF ALUNDUM AS COMPARED WITH PORCELAIN AND PLATINUM

	Alundum crucibles.								Gooch porcelain crucible.		Platinum crucible.	
	1		2		3		4					
	Wt. Grams.	Difference. Mg.	Wt Grams.	Difference Mg	Wt Grams	Difference. Mg.	Wt Grams	Difference. Mg	Wt. Grams.	Difference. Mg.	Wt. Grams.	Difference. Mg.
A	16.2072		12.1658		22.1256		15.4388		19.0030		24.4059	
B	16.2039	—3.3	12.1617	—4.1	22.1194	—6.2	15.4294	—9.4	19.0008	—2.2	24.4055	—0.4
C	16.2018	—2.1	12.1605	—1.2	22.1174	—2.0	15.4290	—0.4	19.0028	+2.0	24.4055	0.0
D	16.2028	+1.0	12.1628	+2.3	22.1193	+1.9	15.4315	+2.5	19.0035	+0.7	24.4056	+0.1
E	16.2032	+0.4	12.1628	0.0	22.1194	+0.1	15.4316	+0.1	19.0035	0.0	24.4056	0.0
F	16.2008	—2.4	12.1600	—2.8	22.1162	—3.2	15.4270	—4.6	19.0007	—2.8	24.4049	—0.7
G	16.2031	+2.3	12.1623	+2.3	22.1182	+2.0	15.4325	+5.5	19.0039	+3.2	24.4059	+1.0
H	16.2031	0.0	12.1623	0.0	22.1188	+0.6	15.4325	0.0	19.0039	0.0	24.4059	0.0
I	16.2007	—2.4	12.1596	—2.7	22.1160	—2.8	15.4286	—3.9	19.0019	—2.0	24.4054	—0.5

crucible and one 30 cc. platinum crucible were used for these tests.

All crucibles were carefully weighed before making this test. They were then ignited in the electric furnace at 1000° C., cooled in a desiccator, and weighed. They were then washed with 250 cc. each of hot and cold water, dried in the electric oven at 100° C., ignited in the electric furnace, and cooled in a desiccator, before weighing. The crucibles were then allowed to stand on the scale pan in the balance case for one, two and three hours respectively. Weighings were made at the end of each period of time. The crucibles were then ignited in the electric furnace, permitted to stand in the atmosphere as before and again ignited for the fourth time. Every conceivable precautionary measure was observed in this test in order that the results might be as accurate as possible. The weights taken of these crucibles at the various stages of the operation are marked by letters, as follows:

A, the original weight of the crucible when received.

B, weight of the crucible after igniting in an electric furnace at 1000° C. and cooling in a desiccator.

C, weight after 250 cc. of hot water had been run through by means of a reverse washer, and 250 cc. run through as in direct filtration, and the crucible dried and ignited in the electric furnace at 1000° C. and cooled in a desiccator.

D, weight after allowing the crucible to stand in the balance case one hour and weighing immediately.

E, weight after the crucible had been in the balance case two hours.

F, weight after the crucible had been ignited in the electric furnace at 1000° C.

G, weight after the crucible had been in the balance case one hour.

H, weight after the crucible had been in the balance case two hours.

I, weight after the crucible had been in the electric furnace and cooled in a desiccator.

The fused alumina is crushed to grains of suitable size, mixed with a ceramic bond, moulded, dried and then fired in an ordinary porcelain kiln. The bond becomes more or less vitrified, forming a hard resistant body. During the process of manufacture small particles of the grain adhere to the outside of the article and are retained in the pores. Upon washing, these small particles are dislodged and washed out. Unless this preliminary precaution is observed an appreciable variation in weight is noted, as shown by the following tables.

TABLE II - EFFECT OF WASHING ON WEIGHT OF ALUNDUM.

Crucible No.	Wt. before washing. Grams.	Wt. after cleaning. Grams.	Loss. Mg.
1	11.6725	11.6708	1.7
2	9.7492	9.7468	2.4
3	11.2629	11.2602	1.7
4	10.0136	10.0094	4.2

Four crucibles were employed. They were weighed, washed with 500 cc. each of hot and cold water, dried in an electric oven at 105° C., ignited in an electric furnace for fifteen minutes at 1000° C., and cooled in a desiccator before weighing. The results are shown in Table II.

After treating these crucibles as above, each was washed with 250 cc. of both hot and cold sulphuric acid, this operation being repeated with hydrochloric acid, 10 per cent. solution. They were then thoroughly washed with distilled water, ignited and weighed. The results of this investigation are summarized in Table III.

TABLE III - EFFECT OF WASHING WITH ACIDS AFTER TREATMENT WITH WATER

	Wt. of crucible.	H_2SO_4, cold	H_2SO_4, hot	HCl, cold	HCl, hot	Total loss
Crucible No. 1	11.6708	11.6702	11.6693	11.6682	11.6668	
	Loss	0.6 Mg.	0.9 Mg.	1.1 Mg.	1.4 Mg.	4 Mg.
Crucible No. 2	9.7468	9.7464	9.7459	9.7458	9.7448	
	Loss	0.4 Mg.	0.5 Mg.	0.8 Mg.	0.3 Mg.	2 Mg.
Crucible No. 3	11.2602	11.2598	11.2592	11.2587	11.2582	
	Loss	0.4 Mg.	0.6 Mg.	0.5 Mg.	0.5 Mg.	2 Mg.
Crucible No. 4	10.1058	10.1058	10.1048	Crucible broken.		
	Loss	0.0 Mg.	1.0 Mg.			

Comparing Table III with II, the necessity of preliminary preparation is demonstrated by the difference in losses suffered due to the several treatments.

IMPROVED TYPE OF FILTER.

A new type of filter, which differs from the crucible, principally in shape and bond, has been recently developed, giving promise of better adaption to analytical work than any other. It differs from the other types of filters mentioned in that it is compact, filters rapidly, and is always ready. It is made from the same materials as the crucibles but is somewhat more resistant to action of the reagents used in ordinary analysis. This new filter is in the form of a cone and is designed to fit into the 60° funnel. One size found satisfactory measures $1^3/_4$" in diameter by $1^1/_4$" high and weighs about ten grams; while this is the most convenient size, the cones can be made up into any desirable shape or size, depending on the specific requirements.

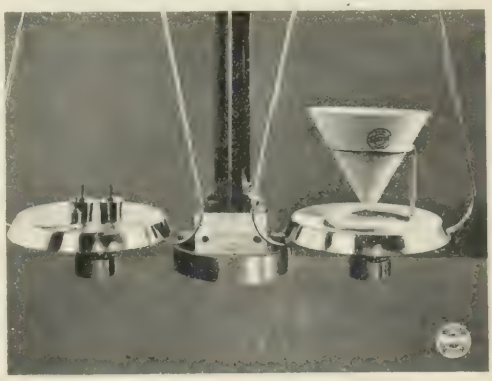

FIG. 2 - FILTER CONE ON SCALE PAN.

This type of filter is placed in operation by first stretching over a large end of the funnel a piece of soft rubber tubing about $1^1/_2$" in diameter and $1^1/_2$" long, allowing half of the tube to project over the top. The funnel is then connected with the filter bottle and the conical filter placed in the aperture formed by the rubber ring. When suction is applied and the filter moistened, the cone is drawn down against

the gasket with a force sufficient to make a gas-tight seal. The efficiency of this joint varies directly with the suction applied. This type of apparatus possesses all the advantages outlined for the best

FIG. 3 METHOD OF ADJUSTING CONE.

laboratory filters. It can be used with or without filter paper, depending on the manipulator and the degree of accuracy required.

When using an ordinary filter paper it may be folded in the usual manner and the point turned back about $^1/_8$" so that the paper may fit snugly into the cone, proceeding then as in the ordinary operation. Several advantages are gained by this method, among them being extremely rapid filtration, depending on the fineness and nature of the precipitate to be filtered. In very accurate work the weight of the cone is independent of the weight of the paper and the cone acts only as a support. It permits the use of a paper whose porosity is suitable for the work in hand.

The entire filtering area of the cone is subjected to the suction so that any and all soluble salts which might be retained by the porous material can be readily removed by proper washing. The advantages resulting from the use of this filter are obvious.

CONSTANCY IN WEIGHT.

The constancy in weight of the cone has been the subject of considerable speculation and discussion. With the idea of determining this under characteristic conditions, the following test was made.

Four cones, of different mixtures, were chosen for this test, namely, RA-320, 321, 322, 327, and were compared with a porcelain Gooch with asbestos mat and an ordinary platinum laboratory crucible.

All of these were soaked in a 10 per cent. solution of sulphuric acid at ordinary temperatures, washed with distilled water and ignited. They were then allowed to stand on the scale pan for one, two and three hours, weighing at the end of each period of time. They were then ignited and weighed, the results being recorded in Table IV.

This type of filter is subject to the same criticism as the other form, namely, the apparent inconstancy of weight, due to the absorption of moisture from the air. As before stated, this characteristic is in no manner detrimental, since the various articles will remain constant when used under the same conditions each time. This fact is illustrated in Table IV.

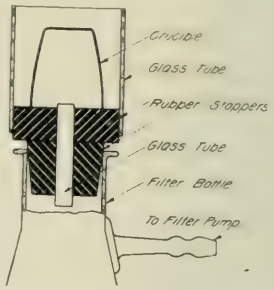

FIG. 4.

The question to be determined is whether they are adapted to quantitative analysis. The favorable results obtained in further tests and recorded in Table V constitute the necessary evidence.

For this final test five conical filters were used and an ordinary porcelain Gooch with asbestos mat. Cones Nos. 1, 2 and 3 were tested without, while cones Nos. 4 and 5 were provided with a lining of filter paper in addition to these a test was made with a filter paper in the usual manner. The 3 precipitates chosen for the test were aluminum hydroxide, barium sulphate and silver chloride, because they are more or less representative of the various classes of precipitates encountered in analytical work. The aluminum hydroxide, barium sulphate and silver chloride were prepared in such a manner as to make standard solutions, 100 cc. of which contained 0.1 gram Al_2O_3, 0.1329 gram $BaSO_4$, and 0.1687 gram AgCl, respectively.

The cones were all thoroughly cleaned and ignited before making this test.

TABLE IV.

Treatment.	Cones 320 Weight. Grams.	Difference. Mg	321 Weight. Grams.	Difference. Mg	322 Weight Grams.	Difference Mg	327 Weight. Grams.	Difference. Mg	Porcelain Gooch crucible. Weight. Grams.	Difference. Mg	Platinum crucible. Weight. Grams.	Difference. Mg.
Soaked in 10% H_2SO_4 and water, then ignited	9.4880		8.0398		5.2539		9.7204		15.6473		11.3184	
Stood 1 hr. in case	9.4893	+1.3	8.0404	+0.6	5.2552	+1.3	9.7216	+1.2	15.6472	—0.1	11.3184	0.0
Stood 2 hrs. in case	9.4893	0.0	8.0408	+0.4	5.2552	0.0	9.7216	0.0	15.6475	+0.3	11.3184	0.0
Stood 3 hrs. in case	9.4893	0.0	8.0408	0.0	5.2552	0.0	9.7215	—0.1	15.6475	0.0	11.3184	0.0
Ignited again.....	9.4881	1.2	8.0398	—1.0	5.2542	1.0	9.7205	—1.0	15.6468	—0.7	11.3183	—0.1

From Table V it will be noted that the first cone was found the most satisfactory for all purposes. The time factor as compared with the Gooch and filter paper was reduced considerably without reducing the accuracy to any appreciable extent.

The cleansing of the filter may be readily accomplished by inverting it on a rubber cork and reversing the flow, as is illustrated in Fig. 4.

On the whole the new conical filters proved to be far superior to those ordinarily used.

TABLE V FILTERING PROPERTIES

	Al_2O_3			AgCl		$BaSO_4$	
Amount found.	Weight. Gram.	Difference Mg.	Time required Min.	Wt Gram	Difference. Mg.	Weight. Gram.	Difference. Mg
By calculation.	0 0500			0 1687		0 1349	
With cone 320..	0 0510	+1 0	2.5	0.1650	3 7	0 1329	—2.0
With cone 321..	0 0510	+1.0	2.0	0 1644	4.3	0 1331	1 8
With cone 327..	0 0502	+0 2	2.0	0 1651	3 6	0 1331	—1.8
With cone 321 + paper ..	0 0522	+2 2	45 0	0 1647	4 0	0 1332	1 7
With cone 322 + paper ..	0 0522	+2.2	30.0	0 1662	—2.5	0 1327	—2.2
With asbestos Gooch..	0 0536	+3 6	11 0	0 1650	—3.7	0 1328	—2.1
With paper filter	0.0519	+1.9	9 0	0.1642	4 5	0 1349	0 0

The authors have endeavored to point out the advantages accruing from the use of a filter of this improved type, the value and superiority of which have already been fully demonstrated by their successful application, under varying conditions, in general laboratory operation.

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CALCULATION OF SULPHURIC ACID STOCK BY APPROXIMATE *vs.* ACCURATE METHODS. A SPECIAL SLIDE RULE FOR THIS PURPOSE.

By H. C. MOORE.

Received May 25, 1912.

When taking periodical inventories of the amount of sulphuric acid stock on hand in the numerous tanks and chambers around a sulphuric acid plant it is customary to test the acid in each tank for density, in terms of degrees Baumé, and also for temperature. The depth of the acid is also measured, and knowing the dimensions of the tanks and chambers it is a simple matter to calculate the number of cu. ft. of acid in each container.

The next step is to calculate, from the data thus obtained, the acid in each lot to the same basis, as, for instance, to the basis of its equivalent in terms of 50° B., 60° B. or 66° B. acid at 60° F. The whole amount of acid on hand is then determined in terms of one grade.

Among fertilizer factories it is customary to calculate all acid in terms of 50° B. acid at 60° F. Tables, which are available, make it possible to determine the number of pounds of 50° B. acid equivalent to a cu. ft. of acid of any density and temperature. The tables as adopted by the Manufacturing Chemists' Association of the United States in 1904 are generally used as a basis for making all calculations.

Now it is no short task for the superintendent or the chemist of a sulphuric acid plant to take a long row of figures, which represent the density and temperature of the acid in the numerous tanks and chambers, and calculate correctly from this data the exact equivalent in terms of 50° B. acid, unless a very voluminous set of tables has been especially prepared for this purpose. By calculating correctly the writer means that exact corrections are made for density and temperature instead of the rough or approximate corrections ordinarily made.

If, however, one is content when taking the acid inventory, to record the density reading to the nearest even degree Baumé and the temperature to the nearest ten degrees Fahrenheit, then the problem is not such a long task, especially if one also assumes that one cu. ft. of acid testing, say, 52° B. at a temperature from 90° F. to 110° F. is equivalent to one cu. ft. of acid testing 53° B. at 60° F. If all of these assumptions are made the summary of the acid inventory becomes very simple indeed, and if a few simple sets of tables have been compiled, practically no calculations are necessary. Such a method of figuring is not correct, however, and the error will vary, being greater for acid at higher temperatures.

Acid testing, say, 50° B. at 130° F. when cooled to 60° F. would have a density of 53.9° B., but one cu. ft. of this acid at 130° F. would have a volume of less than one cu. ft. if cooled to 60° F. while the shrinkage amounts to about 2.25 per cent., or an error too great to be overlooked.

By mentioning the above incorrect methods of calculating sulphuric acid stock, the writer does not wish to infer that such methods are generally used, but has simply referred to some methods which have come to his knowledge both by hearsay and observation. He has also heard chemists remark that they were not sure they were making their claculations with absolute correctness.

There is another slight error which the writer has often observed, which, however, is scarcely appreciable. In the tables adopted by the Manufacturing Chemists' Association, in 1904, will be found a table marked "Allowance for Temperature." This table indicates the correction necessary to apply to Baumé readings to correct from one temperature basis to another. The allowance for temperature for 50° B. acid is 0.028° B. and for 60° B. acid is 0.026° B., for each degree Fahrenheit. Therefore, acids of densities between these limits probably have an allowance-for-temperature value proportionately between the values given. By interpolation the allowance for 52° B. acid would be 0.0276° B. and for 54° B. would be 0.0274° B. for 1° F.

Take the case of acid testing 52.0 B. at 130° F. This acid when cooled to 60° F. would be about 54° B., and, therefore, the value 0.0274 B. for 1° F. should be applied, and 52.0 plus (70 × 0.0274) = 53.9° B. at 60° F. These allowance-for-temperature values were determined, as the writer understands from the original paper on this work, by heating the acid, starting at 60° F. and noting the density variation for rise in temperature. To further illustrate this

point (sp. gr. 1.842) testing 50.00° B. at 60° F. Calculating the density of this acid if heated to 203° F. we get 54.05° B. Now suppose we start with acid at 54° B. and 203° F. and calculate it back to the basis of 60° F. by applying the temperature allowance of 0.0074° B. for 1° F., which, as above mentioned, would be the temperature allowance interpolated for 54° B. acid, and we would get 50.08° B. at 60° F. The discrepancy, of course, is slight, yet it simply points out a very common error which the writer has observed.

To indicate the error in assuming that one cu. ft. of acid at a temperature above 60° F. is equivalent to one cu. ft. of the acid calculated to its density at 60° F. the following table has been prepared:

		Contraction error.
50° B. at 130° F.	= 51.93° B. at 60° F.	2.03
50° B. at 140° F.	= 52.21° B. at 60° F.	2.32
51° B. at 100° F.	= 52.10° B. at 60° F.	1.17
51° B. at 90° F.	= 51.83° B. at 60° F.	0.88
49° B. at 170° F.	= 52.04° B. at 60° F.	3.16
48° B. at 200° F.	= 51.86° B. at 60° F.	3.98
47° B. at 240° F.	= 52.04° B. at 60° F.	5.14

If the amount of acid used per charge when making acid phosphate is measured and the proper corrections are not made for density and temperature, the error will be greater the higher the temperature of the acid used in mixing. Further, if the amount of acid used per week is computed from records thus obtained the error may be considerable. We might assume that the error in calculating the acid in the tanks and chambers is fairly constant from one inventory to another, which assumption would be reasonably correct providing the stock carried in the tanks and chambers remains about constant with small variations in density and temperature.

The writer wishes to state at this point that he is not unmindful of the great difficulty, rather the impossibility, of securing a sample of the acid in the tanks, and especially in the chambers, which is exactly representative of all the acid in each lot. Therefore, the density and temperature of each lot of acid can be only approximately determined. If, however, the acid in each tank and chamber is tested at the same point and in the same manner each time the error will be reasonably constant and the appreciable error, therefore, unless the proper corrections are made as regarding density and temperature, is made in calculating the amount of acid used per week or similar period.

If the acid used at the mixer (acid phosphate) has a temperature of 130° F., the error, resulting by making the incorrect allowance for density and temperature as before described, will amount to about 2 per cent. In other words, the acid department gets credit for 2 per cent. more acid than actually made and the acid phosphate department gets the loss, which is included in the shrinkage allowed.

The writer has known of cases where such errors when unearthed have helped to explain why some acid plants could often get a yield of from 4.95 to 5.20 lbs. of 50° B. acid per pound of sulphur burned.

It might be well to give here two methods by which correct results may be obtained when calculating acid. These methods will not be new to many and yet may be of value to others.

Assume that we have one cu. ft. of sulphuric acid testing 51.0° B. at 100° F. and wish to find its equivalent in terms of 50° B. acid at 60° F. First by reference to the tables and making the calculations before described, we calculate that this acid would have a density of 52.1° B. at 60° F. From this point the calculation may be made by two methods:

Method I:

1 cu. ft. 51.0° B. acid weighs 96.21 lbs. (from table)

1 cu. ft. 52.1° B. acid weighs 97.35 lbs. (from table)

96.21/97.35 = 0.9883 cu. ft. = volume which the cu. ft. of 51° B. acid at 100° F. would have if cooled to 60° F.

1 cu. ft. 52.1° B. acid at 60° F. = 102.20 lbs. 50° B. acid (interpolated from tables).

Therefore, 0.9883 × 102.20 = 101.00 lbs. 50° B acid at 60° F.

Method II:

1 cu. ft. 51° B. acid weighs 96.21 lbs.

52.1° B. acid at 60° F. = 104.98 per cent. of 50° B. acid at 60° F. (interpolated from tables).

104.98 per cent. of 96.21 = 101.00 lbs. 50° B. acid at 60° F.

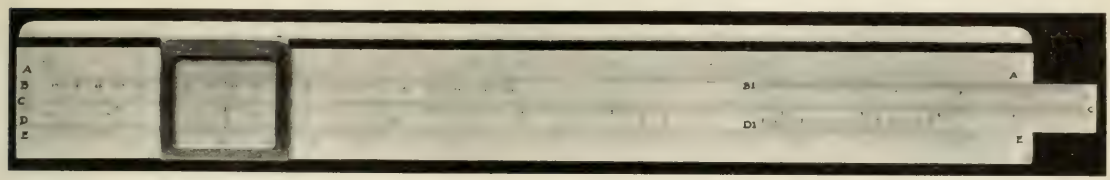
Method I though longer than Method II is interesting in that it will indicate the shrinkage in volume which would result if the acid were cooled to 60° F.

The writer has seen private sets of tables which have been compiled and which make all necessary corrections, thus greatly shortening the time required in making the calculations of acid of different densities and temperature to one basis. At one time he also prepared such a set of tables, but the time required was about three weeks, and the tables then were not thoroughly complete but fulfilled practically all the requirements of the plants at which they were used.

It then occurred to me that some simple means might be found for making all such corrections and calculations in a short time, so my efforts were directed to the problem of determining if it were possible to design a special slide rule by means of which all calculations might be made. After spending considerable time a design for such a slide rule was finally devised and after making many hundred calculations the full details and specifications were worked out. Models were then prepared, which proved that the rule would permit accurate calculations to be made.

By use of this slide rule corrections may be applied to Baumé readings for temperature, thus calculating acid of one density to corresponding density at any other temperature. This requires one adjustment only of the slide rule. Now by making one additional adjustment the final result may be read from the rule directly; that is, one cu. ft. of acid of any density and temperature can be calculated to its equivalent in terms of 50° B. acid at 60° F. (or in terms of 60° B. or 66° B. acid if desired, or in fact to any basis). Also, if desired, 100 lbs. of acid of any density and temperature can be calculated to its equivalent of 50° B. acid at 60° F. (or to any other basis desired) just as easily.

Each case can be worked out by means of this rule in less than ten seconds, which surely allows a wonderful saving of time. The rule is based entirely on the tables of the Manufacturing Chemists' Association of the United States, adopted 1904, and no tables need be used in connection with the rule to give final results.



The accompanying cut shows one of these slide rules, submitted by the manufacturers as a sample, but which is not exactly correct.

The divisions on the slide rule are marked in terms of degrees Baumé, degrees Fahrenheit and pounds per cu. ft. Baumé divisions are to tenths, and in some cases to 0.05° B., the Fahrenheit scale to 1° and the pounds per cu. ft. scale to tenths of a pound per cu. ft. The latter scale can be read to within 0.01 to 0.02 lb. per cu. ft. and the Baumé scale to 0.01° B. In other words, the accuracy of results obtained by the rule are within the limits of error of reading an ordinary hydrometer divided to tenths of a degree Baumé. The scales include Baumé readings between 48° and 66° B. and from 30° to 160° F.

Referring to the rows of divisions by letters: Row D^1 and E are used together to correct Baumé readings from one temperature to another.

Row B^1 is a continuation of Row C, which is likewise a continuation of Row D. This arrangement is adopted to get all of the divisions on a 10" rule and yet have divisions far enough apart to permit accurate and rapid readings. The value of divisions in these rows represents pounds per cu. ft.

Row B is divided in terms of weight per cu. ft. of acid of different densities. To find from this rule the weight per cu. ft. of acid of densities between the limits included, refer to the division on Row B corresponding to its Baumé reading and project on to Scale C, where the value for its weight can be directly read.

Row A is divided in terms of percentages. (Attention is hereby called to the error on this row, noticeable between the 49 and 50 divisions.) To find the per cent. of one acid as compared to 50° B. acid, adjust the slide so that the 50 division, Scale A, is in vertical alignment as indicated by the runner with 100 on Scale C. Now adjust the runner over the division on Row A corresponding to the density of the acid which it is desired to refer to its per cent. of 50° B. acid and read below on Scale C. To find the corresponding per cent. of 60° B. acid, the operation is similar.

To calculate, for example, 1 cu. ft. of acid testing 51.0° B. at 100° F. to its equivalent in terms of 50° B. acid at 60° F. by this rule, the procedure is as follows:

Line up, by means of the runner, division 100 on Row D^1 and division 51.0 on Row E. Now move runner to division 60 on Row D^1. Read below on Row E and 52.1° B. is indicated as the corrected Baumé reading. Now adjust the slide so that division 50, Row A, and division 51, Row B, are in alignment. Move the runner over the 52.1 division on Row A and read under the runner on Row C, when 101.00 is indicated as the correct result.

Such a slide rule would be of very great value to a chemist or superintendent who has to calculate sulphuric acid stock, and also to a broker who buys and sells acid.

ARMOUR FERTILIZER WORKS,
ATLANTA, GA

A SIMPLE AND INEXPENSIVE CONDUCTIVITY CELL.

By CARL A. NOWAK.

Received June 8, 1912.

Unable to obtain a standard conductivity cell from any of the chemical supply houses in town, and anxious to complete a series of experiments, the author undertook to construct a cell from materials available in the laboratory. This cell, although primarily intended as a makeshift until a standard cell could be obtained, gave such satisfaction, that, for the experiments in hand, it proved practically equal to any of the standard cells now on the market. A brief description of the manner in which this cell was constructed may possibly be of assistance to others, who, like the author, may at some future time be dependent upon a cell of their own construction.

Before going into details it may be well to point out certain of the advantages possessed by this cell: *First*, It requires only 20 cc. of liquid. *Second*, On account of the small volume of liquid the same is more quickly brought to the temperature of the thermostat. *Third*, The cost is considerably lower than that of the cells on the market since the electrodes are made of thin platinum foil, but being concave and themselves fastened directly into the cork cover, are rigid and not easily bent out of shape or otherwise injured, thereby causing a change in the cell constant. *Fourth*, The cell constant can be adjusted to suit the requirements of the test, either by varying the height of the liquid or by reducing the electrode surfaces. The thermometer is directly in the path of the electrodes, and the two loops of platinum foil make it very easy to connect the cell to the circuit. The complete cell can be easily constructed in about one hour from materials to be found in almost every laboratory, and at a low cost.

Fig. 1 is a photograph of the cell and Fig. 2, diagrams giving better the details of construction.

A wide mouthed glass bottle $1^1/_4$ inches in diameter and $2^1/_4$ inches high was used for the cell body. A

flat cork of a somewhat greater diameter than that of the bottle and about $^3/_8$ of an inch thick was next selected and a disc a little less than 1 inch in diameter cut out of it by means of a sharp penknife, care being taken to cut perpendicular to the surface of the cork and neither to injure the disc nor the ring which remains as the disc must be replaced in the cork after the electrodes and contact strips are inserted. Two pieces of platinum foil 0.002 inch thick, 1 inch wide and 2 inches long were cut, as well as two strips of the same foil two inches long measuring about $^1/_8$ inch in the center and $^3/_8$ inch at the ends, cut in the manner

Fig. 1.

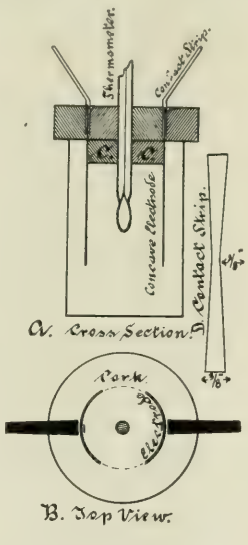


Fig. 2.

shown in Fig. 2, D. The strips were each folded over in the middle so as to form a loop, the ends being then fastened between the ring and the disc of cork together with the two electrodes in the manner shown in the illustrations.

The tops of the electrodes should come flush with the top of the cork. If the cork has been properly cut, the electrodes, owing to the now concave shape, will hold firmly in the cork and should be parallel to one another (see Fig. 2, A). Should this, however, not be the case, a short round piece of cork (Fig. 2, C), previously shaped to fit, can be placed between the electrodes and cemented to the cork proper with the aid of a little plaster of Paris.

The cork is now covered with sealing wax on all sides which gives excellent insulation. This can be made smooth by passing a hot, flat piece of steel over it. A knife blade answers very well. For safety's sake, and to prevent short circuit, should any liquid accidentally get on the stopper between the electrodes, the same is dipped into melted paraffine, the loops being again scraped free.

A more finished looking cell can be made by applying plaster of Paris to the cork after inserting the electrodes, instead of the sealing wax. The plaster can be sandpapered down after drying, giving a perfectly smooth surface and covering all imperfections in the cork. If the same is then coated with black enamel or paint the entire cell has a very neat appearance. Of course the cork must be subsequently dipped in paraffine for the reasons given above.

After cleaning the electrodes carefully, the same are coated with platinum black in the usual manner.

The opening for the thermometer is most easily made by heating the point of a round file to redness in the Bunsen flame and then applying it to the cork with a slight pressure, thereby easily penetrating through the sealing wax and cork. After this has been done, the opening in the cork can be filed out by means of the same file, until the thermometer exactly fits it. The author made use of a pycnometer thermometer divided into tenths of a degree and reading from 10° 30° Centigrade.

The general type of the cell, *i. e.*, concave electrodes, makes it especially well adapted for use with poorly conducting fluids, the cell constant of the cell illustrated being 0.237 when 20 cc. of liquid are used.

In using the cell and for determining the cell constant, 20 cc. of liquid are measured into the glass from a standard pipette (always used for this purpose). It will be found that in dealing with the same kind of solution, *i. e.*, one of uniform viscosity, the cell constant will remain unchanged within the permissible limits of error allowed in technical conductivity measurements, provided of course that the same pipette is always used for delivery.

Should one so desire, other volumes of liquid may be used, *viz.*, 30, 15 and 10 cc., the cell constant being determined for each of the respective heights of liquid in the cell.

The cell is very easily cleaned, simple in manipulation and not easily damaged.

2739 Mildred Ave.,
Chicago.

APPARATUS FOR FUMELESS KJELDAHL NITROGEN DIGESTION.

By A. P. Sy.

Received June 4, 1912.

A digestion with sulfuric acid for the Kjeldahl nitrogen determination is practically impossible unless some provision is made for taking care of the large volume of fumes evolved. Even in small quantities these fumes are so objectionable that complete removal is necessary. Many devices and arrangements are known and in use, the customary practice being to conduct the digestion in a good hood or closet connected with an efficient natural or forced draught. Such an arrangement is often almost impossible and is always expensive, necessitating an expenditure of several hundred dollars when a fan and motor are used. In addition to the expense, this arrangement is always very noisy, unless the fan is located at some distance from the hood, in which case its efficiency is decreased proportionately. For a number of years the writer used a hood with natural draught, but on some days it was necessary to open all windows and leave the room. Many laboratories, especially those of hospitals and physicians, have no fume closets at all and a

Kjeldahl nitrogen digestion is out of the question. Three years ago the writer began using an arrangement similar in principle to the one here described and shown.

FIG. 1. FRONT VIEW.

It has been in constant use in the university as well as the writer's laboratory, and in its present form seems to answer all requirements for fume absorption.

A brief description and reference to Figs. 1 and 2 readily explain the apparatus. The whole is mounted on a portable iron stand, occupies but a little space and is easily moved. In the apparatus here shown, four ordinary long-necked 500 cc. Kjeldahl flasks, suitable for digestion and distillation, are used.

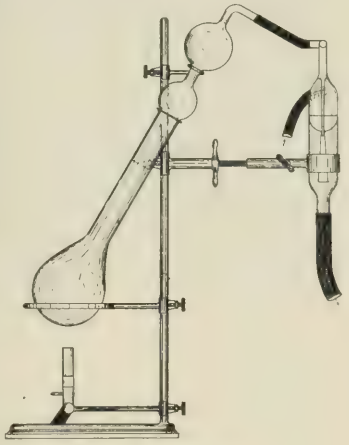


FIG. 2. SIDE VIEW.

The Kjeldahl flasks are supported at the bottom by a special ring-clamp. Into the neck of each flask there is a loosely fitting bulb-tube with two large bulbs and an elbow bend. These bulb-tubes are connected with a large glass suction pump having four branches. Rubber tubing is used for connecting the bulb-tubes and pump, in order to give flexibility to the apparatus, allowing the flasks to be shaken without detaching them. The rubber tubing lasts for many determinations and can easily be replaced. The bulb-tubes are held in position by a special support, allowing their easy removal when shaking is necessary. The bulbs act as air cooled condensers for the acid fumes, and prevent the materials in the flasks from going dry as quickly as when the fumes are allowed to escape. The lower bulb acts as a loose stopper for the flask, while the upper one rests on the support when the apparatus is not in use, always leaving the bulb tubes in position. At the beginning of a digestion, water is driven off, and in order to prevent its dropping into the hot acid and causing spurting, the supports of the Kjeldahl flasks are so arranged as to give the latter a slanting position, allowing the condensed water to flow down the sides gradually. In its present form the apparatus has a quadruple burner on a clamp attached to the iron stand, as shown in the drawings. To operate, connect the pump with the water supply and drain, and start heating the flasks with a low flame. The operation and advantages of this arrangement need no further explanation. The apparatus may be obtained from Eimer and Amend, of New York City.

UNIVERSITY OF BUFFALO,
BUFFALO, N. Y.

A SIMPLE METHOD FOR PURIFYING DRINKING WATER.

By J. L. SAMMIS.

Received July 10, 1912.

Water for drinking purposes is commonly purified on the small scale by distillation. Distilled water is flat and unpalatable and has to be cooled and stored for use.

The possibility of pasteurizing water for drinking purposes, as it flows from the pipes, seems to have attracted little attention. For this purpose, water flowing through a small pipe can be momentarily heated (in a steam jacket or otherwise) to a temperature of 175–180° F. (79–82° C.), by which means disease germs such as those producing typhoid fever, dysentery, etc., are destroyed, while the water under pressure in the pipe does not lose its dissolved gases or its palatability.

The water thus heated can be quickly cooled in the pipe, by means of a cold water jacket. In most buildings, only a small proportion of the water used would require to be heated and cooled for drinking purposes, but the entire quantity used for all purposes could be run through the jacket, to aid in the cooling.

An arrangement of pipes for this purpose can be set up by any pipe fitter at any point where a steam pipe and a water service pipe pass near each other. It is desirable that the steam pressure be uninterrupted, and that the pipe be drained free from condensation. Also the water pipe should be one through which more or less water is flowing continually. The diagram shows the arrangement of the parts.

The steam main is cut at A A′, the water main at B B′, and the cut ends are reconnected through by-passes which constitute the steam jacket C, and the water jacket D, used for cooling the drinking water.

A small stream of water is drawn from the main through valve O, passing through the small jacket P, where it partly cools the water in the interior coil M. From the jacket P, the water flows through V and upwards through K within the steam jacket C, where it is heated to 180–200°F The heated water flows past the thermometer T, through the coil M, and finally into the cooling coil of the water jacket D. The water thus heated and cooled flows out below, when the faucet X is opened, either into a cup or into a bubble fountain.

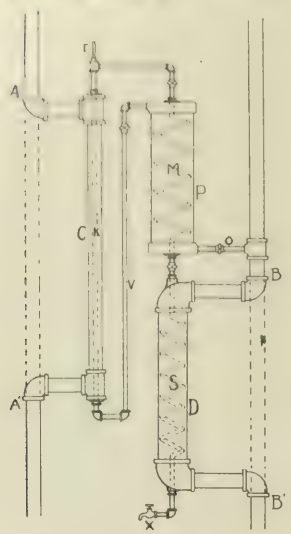


FIG 1.

Very efficient cooling can be secured by making coils M and S of tin lined brass pipe. These can be of thin material, since the water pressure inside and outside of them is always alike. In practice, with such an arrangement, no difficulty was found in cooling the water for drinking to within 2° of the temperature of the cooling water in the jacket D. For some reason, not well understood, the water thus heated and cooled under pressure is more palatable to some observers than the untreated water supply.

The water pressure should be about 25 pounds greater in the main B, than the steam pressure in A, in order that the water may not boil in the pipe K, which may be made of $^1/_4$ or $^3/_8$ inch galvanized or tinned iron pipe.

In cities where the municipal water supply is known to be contaminated with sewage, causing typhoid fever, the pasteurization of water as it flows from the pipes for drinking purposes appears desirable.

In large office buildings, factories, schools, etc., where steam pressure is maintained throughout the summer, and where water flows continually through the mains for supplying toilet rooms, work rooms, etc., such an arrangement for pasteurizing water for drinking purposes might find useful application.

The amount of steam used in such an apparatus is small, because the regenerative cooler P prevents waste of heat.

For residences, either gas or electric heat might be substituted for steam in such an arrangement as the one described above.

UNIVERSITY OF WISCONSIN,
MADISON.

SAMPLING CONE.

BY C. W. KNEEP.

Received May 28, 1912.

Every one who does ore sampling has noticed that the lumps always roll to the bottom of the pile, when the ore is piled in the form of a cone preparatory to quartering. When the cone is built up by placing shovelfuls of ore on the apex of the cone, this is unavoidable and segregation of lumps and fines always results. By the use of a hopper such as is shown in the sketch, this condition can be almost entirely overcome. The ore is shoveled into the hopper, and allowed to run through the hole in the bottom; each piece of ore remains practically where it falls and when the pile is flattened out for quartering there is no segregation of coarse and fine to be seen.

The sketch shows a 1 inch hole in the bottom of the hopper, but for some work it should be larger, *e. g.*, for coke, which has a tendency to choke the opening and stop operations. For general work I find a hole

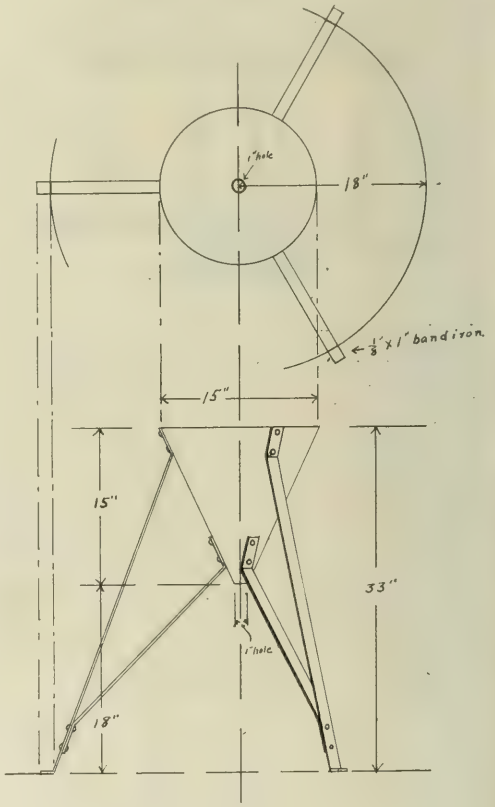


FIG. 1. CONE FOR SAMPLING ORE.

of $1^3/_8$" diameter most satisfactory, but I have some funnels with smaller openings, which I can drop inside the main funnel, and obtain any size of opening desired.

As the sample comes from the crusher, the largest piece is about $^3/_8$ inch and is mixed with considerable fines. This is passed through the hopper three times, which gives a very uniform mix, much better than can

be obtained by the common practice of piling with a shovel. After quartering, the portion retained is passed through the cone again, and so on till the sample weighs from 8 to 10 pounds, after which it is passed through a No. 8 sieve and finished in the usual way.

SHOENBERGER STEEL WORKS,
PITTSBURGH, PA.

A LABORATORY GLASS-FURNACE.

By S. R. SCHOLES.

Received June 17, 1912.

Experimental glass-making has always been attended by the difficulty of getting the necessary temperature. We have installed in this laboratory a furnace burning natural gas and using the regenerative principle common in glass-factory practice. The designing and construction of this furnace, following our rough sketch, were undertaken by Messrs. Armstrong and Lytil, furnace builders, of Pittsburgh.

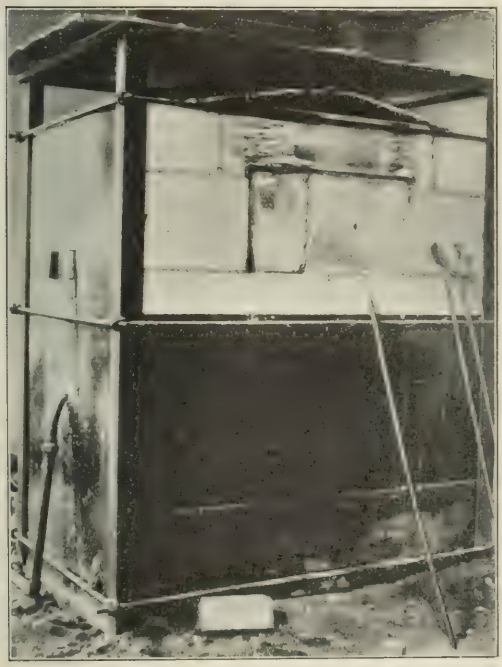


FIG. 1

The accompanying photograph gives an idea of the general plan of this furnace. It is constructed of standard sizes of furnace blocks. An arched roof of silica brick covers a crucible bench 42 × 27 inches, at the ends of which the gases enter from the vertical regenerators, through openings 9 × 12 inches There is thus a space accommodating several crucibles of generous size, such as size "M" of the Battersea make. The regenerator columns enlarge below the bench to $16^1/_2$ × 21 inches and are 4 feet high. They are filled with the usual silica checker brick. From the foot of each regenerator a horizontal flue leads to the stack and connects by a suitable valve with an air inlet. A twenty-five-foot stack is used.

Gas is supplied through one-inch pipes, under a pressure equal to eight inches of water. The gas is not "regenerated" but enters, through a three-eighths-inch nozzle, into each regenerator column just below the level of the bench.

The furnace can be brought from room temperature to its full heat in about twelve hours. It is usually maintained at 1350°–1400° C. but a higher temperature can easily be reached, which is practically limited by the softening of the crucibles. The best efficiency is obtained by reversing gas and air supply every twenty minutes. The gas-consumption is about 250 cubic feet per hour.

Much of the credit for the design of this furnace is due Prof. S. L. Goodale, of the School of Mines.

INDUSTRIAL RESEARCH LABORATORY,
UNIVERSITY OF PITTSBURGH.

THE DETERMINATION OF CARBON IN STEEL BY DIRECT COMBUSTION IN THE NEWEST FORM OF SHIMER CRUCIBLE, WITH THE AID OF A PERFORATED CLAY DISC.

By FRANK O. KICHLINE.

Received May 31, 1912.

In THIS JOURNAL, for October, 1909, Dr. P. W. Shimer described a simplified form of his crucible for the determination of carbon in steel by combustion. Two improvements have been made in the use of this crucible for direct combustion. These improvements are (1) an increase in the diameter of the crucible, and (2) the use of perforated clay discs instead of asbestos for covering the charge of drillings.

It has been the practice, in the direct combustion of carbon in steel, to place the drillings in a No. 000 Royal Berlin porcelain crucible two-thirds full of silica sand, placing this porcelain crucible inside of the Shimer platinum crucible with a pair of forceps, and covering the charge with a layer of ignited asbestos about $^3/_4$ inch thick. The asbestos serves to keep the drillings in place and prevents heat radiation to the water-cooled stopper.

A slight increase in the diameter of the Shimer platinum crucible made it possible to use a No. 00 Royal Berlin crucible instead of the No. 000 size. The No. 00 size has at the top an area 1.41 times that of the No. 000 size, and is filled to only one-half its depth with silica sand. This has the obvious advantage of permitting the use of a heavier charge, full factor weight (2.7273 g.), or if the $^1/_2$ factor weight is preferred it will be less crowded. Dr. Shimer has recently adopted this increased diameter for his standard size crucible.

Ignited asbestos as a covering for drillings is very efficient. While results are not vitiated by the presence of ignited asbestos, it is obvious that the packing in of a layer of asbestos before each burning, and its removal after burning, are both time-consuming and inconvenient, and the source of much dirt around the carbon work table.

In trying to obviate the use of asbestos, the writer

tried various materials made up into the form of discs with perforations for the circulation of oxygen. The best results were obtained with a disc about $^{5}/_{16}$"

CLAY DISC.

thick, of such diameter as to completely cover the No. 00 Royal Berlin porcelain crucible, perforated with slanted holes, leading from the periphery of the upper side of the disc, slanting toward the center on the bottom of the disc, as shown in the illustration. They are best made of china clay. The clay is mixed with water to the proper consistency, moulded into shape, carefully dried, burned and annealed. One of these discs with proper care will last for 100 determinations, which is also the average life of the porcelain crucible. With a little care these discs can be made easily in the laboratory.

The above work has been carried on by the writer in conjunction with Dr. Shimer.

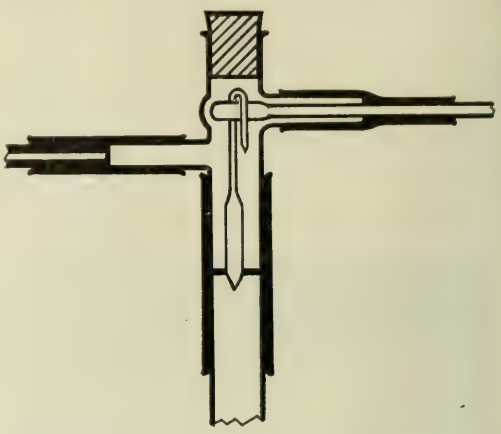
35 First Avenue,
Bethlehem, Pa.

A MODIFIED VICTOR MEYER APPARATUS.

By Harold Canning Chapin.

Received June 24, 1912.

The customary way of introducing a liquid to be vaporized in a Victor Meyer vapor density apparatus is to drop, by some external means of control, a capsule previously supported in the cool upper portion of the tube. This capsule then automatically releases its contents by bursting, expulsion of a glass stopper, or melting of a Wood's metal plug. The first method is preferable, but requiring a completely filled, fragile capsule, is somewhat troublesome. A modification of this, having proved successful with a class of engineering students in this laboratory, seems worthy of more general use. The capsule is made from a piece of 5 mm. tube sealed off at one end and drawn out to a capillary at the other. It is filled to the neck only, bent as shown, and sealed at the tip of the capillary. It is hung in the vaporizing tube instead of being supported in the usual manner from below. For this



purpose the ordinary form of tube will serve, but the right angled form here illustrated is preferable because it is more compact, holds the capsule more securely, and allows this to be placed in position more easily through the short neck. A twist of the rod with its flattened end breaks the capillary and drops the capsule.

Walker Laboratory,
Rensselaer Polytechnic Institute,
Troy, New York.

ADDRESSES

THE ANALYST VERSUS THE CHEMIST.[1]

By J. S. Brogdon.

Received July 15, 1912.

There is no subject of greater importance in the fertilizer world to-day than that of Chemical Economy. The chemical units of phosphoric acid, nitrogen and potash in the fertilizer factory are the same as and are equivalent to dollars in the bank. In all the nation you will not find a single bank which for one moment would think of doing business without an efficient and adequate method of keeping account of the money, or without a banker to direct the policy of the bank. Yet in fertilizer factories, systems for keeping account of the income and the outgo of chemical units are not common, and many factories are not under the direction of a chemist. As a result, in the average fertilizer factory, there is a most wanton waste of phosphoric acid in the manufacture of acid phosphate and in the manipulation of mixed fertilizers the losses frequently exceed the profits. To a large extent these losses are caused by improper chemical control or the lack of it.

The days of large profits and splendid dividends in the fertilizer world are over. A new era has dawned—a time of keen competition and close margins—a time when it is necessary that the smallest savings be effected. The wasteful methods of the past cannot be continued and the standard of the quality of the product must be maintained. There is no greater avenue to prosperity for the fertilizer manufacturer than that of applied chemistry. The question naturally arises, who shall apply the principles of chemistry in the fertilizer industry?

Fertilizer managers are occupied with the matter of sales and credits: frequently they are men who have risen from the ranks of the sales force and their training has not fitted them to handle the intricate chemical problems of the factory. On account of this they are accustomed to rely on fertilizer superintendents to look after such matters. The superintendent most

[1] Read before the Convention of The National Fertilizer Association at Atlantic City, July, 1912

frequently is a man who has been promoted from the manufacturing department and often has not given the subject of chemistry as careful consideration as he has the matter of efficiency of machines and the control of labor. It matters little whether this knowledge which we call chemistry is obtained at the fountain head in the factory or through the canned source of text books. It is very important that if a man possess this information, it be harmonized and organized. "Science is organized knowledge." The science of chemistry offers two fields for investigation: analytical chemistry, which takes things apart, or separates them into their component parts, and synthetic chemistry which takes substances and puts them together to form new substances. The man who understands the principles of analytical chemistry and synthetical chemistry and has the ability to apply these principles in a fertilizer factory is a man most worthy of the name of chemist.

The trouble in the application of chemical principles in the fertilizer industry can most frequently be attr buted to the fact that managers and superintendents confuse the services of an analyst with those of a chemist. A man who possesses certain chemical information and who is skilled in the manipulation of fancy pieces of glassware and who can perform certain cook book operations, as furnished him by the government, is an analyst. He is capable of disintegrating substances and can express the relation of the component parts in terms of percentages. In other words, an analyst is a man who undoes things; a chemist is a man who does things. It would be well if all chemists were analysts and it is a deplorable fact that all analysts are not chemists. If you have samples to be analyzed, send them to an analyst, but if you have chemical problems to be solved or dividends to be saved, consult a chemist; let him apply the principles of chemistry.

Under the head of Applied Chemistry perhaps there is no question of greater importance in the fertilizer factory than the manufacture of acid phosphate, and it is in an instance like this where the chemist does not receive credit for his labors. A pile of acid phosphate may run 2 per cent. insoluble and look exactly like another pile which runs only $^1/_2$ per cent insoluble. Yet the loss in this case would be $1^1/_2$ per cent. or something like 75 cents a ton. The work of the chemical engineer is not appreciated because it is intangible. A chemical engineer can produce profits which frequently are not audited.

A certain fertilizer factory installed a chemist in their acid phosphate department and at the end of the first year he effected savings which amounted to $20,000; at the end of the second year the auditor credited this department with savings of $40,000 over the old system, and at the end of the third year he was credited with savings of $60,000 over the old system. In the meantime, the quality of the product which at the first had been none too good, had now become recognized as the best on the market. This was the work of a chemist.

A careful and systematic analysis of all raw materials and mixed goods is an advantage that is not appreciated by every manager. Again, the chemical units can be compared to money. Any man will count his money regularly and systematically, yet the same man does not think it necessary to count or audit his chemical units systematically. The matter of 25 cents per ton profit is not to be scorned. If there is a variation in the quality of the materials, it is usually practical and possible to vary the formulae accordingly. This varying of formulae, however, becomes confusing and impossible if the materials have not been properly stored in the shed. Many manufacturers consider that all that is necessary is to unload the material. This is, indeed, a very poor way to handle the matter. Where large quantities of fertilizer materials are being handled, some one should be delegated to know at all times how these materials are stored in order that they can be used to their highest chemical efficiency.

The chemical control of the manipulation of mixed fertilizers is a subject which has been sadly neglected and which amounts to losses of many thousands of dollars per annum. In no other industry is the custom prevalent to give 37 inches for a yard as in the fertilizer world, and frequently the manufacturers of commercial fertilizers are not satisfied with giving away their goods, but they actually throw them away. A loss of $1.50 a ton in averages in a fertilizer factory in the city of Atlanta was reduced to 44 cents per ton through the agency of chemical control. This saving amounted to about $15,000 in one season. This was the work of a chemist.

The packers and the large interests have long since realized the importance of chemical economy and have delegated these responsibilities to a chemist. The independent plants frequently employ a chemist, or rather they maintain a laboratory and pay a man a salary to make chemical analyses, preferring that he occupy his time in this way. Unless there is some one in the factory to interpret the certificate of analysis and apply the principles, the whole procedure becomes a farce. Frequently fertilizer managers fail to consider their chemist in the light of a professional man as they do their lawyer, and superintendents look upon the chemist as a kind of necessary nuisance whom they tolerate rather than seek.

From the early days of Liebig to the modern times of Cameron and Whitney, the devotees of the pure science of chemistry have applied themselves to the study of the nutrition of plants. The chemical engineers have done all in their power to foster the fertilizer industry and have met conditions nobly. I refer to such men as the elder Grasselli who conceived, built and operated the plants of the firm that bears his name. The splendid results of Mr. Herrescholl attest to his interest and ability. All over the South are modern plants which were designed and built by Nathaniel P. Pratt, and at all times the chemical profession has met conditions and now stands ready to meet this new condition, the necessity for chemical economy.

65$^1/_2$ North Broad Street,
Atlanta, Georgia.

CURRENT INDUSTRIAL NEWS

By W. A. Hamor

FACTORY INSPECTION.

The *Blue Book* containing the annual report of the Chief Inspector of Factories and Workshops for 1911 has just been issued in London, and its contents should prove of great interest to those engaged in the study of industrial diseases. According to the *Chemical Trade Journal*, 51, 4, the points of special interest to the chemical trades dealt with in the report are the following:—

Regulations for Dangerous Trades.—The regulations for the smelting of lead material, etc., render obsolete the special rules for lead smelting and for the manufacture of red, orange and yellow lead. Subject to certain exemptions for materials containing negligible quantities of lead, the code requires the suppression or removal of dangerous dust or fumes; the provision of overalls and respirators in certain processes; the exclusion of persons under 16 years of age and females from lead processes; the exclusion of persons from furnaces, etc., until ventilated; the restriction of the duration of work in flues and condensing chambers; the provision of meal rooms, etc.; and the periodical medical examination of workers in lead processes.

Chemical Works.—Hilditch states that although vats and pans containing liquid of a dangerous character are being fenced in conformity with Rule I, yet the deleterious action of acid fumes upon the stanchions and rails requires careful and periodical examination. Workmen frequently place a plank across a full vat to save themselves the trouble of going around or between pots. Dunolly, owing to two fatalities, gave special attention to the fencing of the waste liquor settling tanks of ammonium sulphate plants. These tanks are about 5 feet deep, and are divided into two sections which are alternatively filled with the boiling waste liquor through a special by-pass channel. He explains that only one section—the one containing the hot liquor—is really dangerous, but the two workmen happened to fall into that tank.

Benzene Derivatives.—Last year one case of dinitro-benzole poisoning was reported, and it was thought that by the careful selection and timely suspension of workmen by appointed surgeons, the cases could be reduced to a minimum. This year, however, 23 cases were reported. These were due to an exceptionally warm English summer, with the consequent greater absorption of the poison by the more open pores. The method of manufacture is said to be still primitive, and more automatic working in places laid with impervious washable floors is considered essential. An improved method of breaking up cake, enclosing of apparatus as much as possible, and provision of much stronger exhaust, are urged as remedies. There were three cases of skin disease reported in 1911 as against 16 in 1910; one case of eczema and one of dermatitis from a factory in which dinitrochlorbenzole is made; and two cases of aniline absorption among workmen in a factory where cotton cloth is dyed.

FACTORY VENTILATION.

It is stated in *Popular Mechanics*, 18, 202, that the heating and ventilating equipment of a new factory building in Springfield, Mass., includes two air-cooling machines of the water-spray type. The air is taken in through an opening in the pent house, enters the cooling machine, is drawn through the water spray, passes a number of baffle plates, continues through the fan into the stair well and passes from there through the louvers into the workrooms. After it has circulated through a workroom it leaves through the upper louvers in the center partitions and is drawn into the main stair well. The water for the machine is taken from the well at a rate of about 60 gallons per minute for each machine and at a temperature of about 54° F. The manufacturers guarantee that air entering at 95° F. and containing 9.3 grains of water to the cubic foot will be cooled to 78° F. It is calculated that under these conditions it will be possible to keep the temperature inside the building about 9 deg. lower than the outside, changing the air four times an hour.

MERCURY POISONING.

A report on "Mercury Poisoning in the Industries of New York City and Vicinity," by Mrs. L. W. Bates, has been issued by the National Civic Federation. Outside of felt hat manufacture, the industries using mercury are not extensive; they are very limited within a radius of fifty miles of New York City. In hatters' fur cutting, a solution of mercury nitrate is employed in carotting, and mercury poisoning is likely to happen in the subsequent process of cutting and brushing by inhalation of particles of fur impregnated with nitrate of mercury. Neither mercury nor any of its salts is used in hat making proper: mercurialism results from the earlier treatment in carotting, yet much more poisoning occurs in the hat making than in the fur cutting processes, owing to the mercurial dust disseminated in certain operations of hat making (blowing, forming, hardening, and sizing). Cases are cited and experiences are recorded to show that mercury is manifestly a poison which, in occupations, is inimical to health and calls for regulation. Mrs. Bates concludes that the unhealthy nature of the trade should be placarded; that eating and drinking should be forbidden in rooms where mercurial processes are conducted; that ample washing facilities should be installed; that proper drinking water should be supplied; that sweeping should be superseded by vacuum cleaning; that the mixing of mercury and acids should be done after working hours; that rubber gloves and respirators should be supplied; that the hat industry should be regulated by special legislation, requiring the elimination from the atmosphere of steam, heat, acid fumes and mercury vapor, fur and dust, at their source of production; that regular medical inspection should be provided; and that compensation and insurance should be supplied for the men working in these processes.

SPECIFICATIONS FOR REFRACTORIES.

The Refractory Material Committee of the Institution of Gas Engineers in their annual report deals with silica bricks, blocks, tiles, etc. (see *J. Gas. Ltg.*, 118, 828). The materials covered by the standard specifications are divided into two classes, namely:

1. That containing 92 per cent. and upwards of silica, and termed "silica" material.

2. That containing 80 to 92 per cent. of silica, and called "siliceous."

The requirements of each class of refractory materials follow.

Refractoriness.—Test pieces of the material shall show no sign of fusion when heated to the following temperatures: "Silica" material—not less than Seger cone 32 (about 1710° C.). "Siliceous" material—not less than Seger cone 29 (about 1650° C.). It is required that the test shall be carried out in an oxidizing atmosphere, the temperature of the furnace being increased at the rate of about 50° C. per 5 minutes.

Surfaces and Texture.—The materials shall be evenly burnt throughout and possess a regular texture; there shall be no holes or flaws, and all surfaces shall be reasonably true and free from flaws or winding.

Contraction and Expansion.—A test piece, when heated in a

gas-muffle or electric furnace to a temperature of Seger cone 12 for 2 hours, shall not show, on cooling, more than 0.75 per cent. linear contraction or expansion.

Variations from Measurements.—In the case of ordinary bricks, 9 in. × $4^1/_2$ in. × 3 in. or $2^1/_2$ in. thick, there shall not be more than about $1^1/_2$ per cent. variation in length, nor more than about $2^1/_2$ per cent. variation in width or thickness; in all cases the bricks shall work out their own bond.

THE UTILIZATION OF SULPHITE LIQUOR.

The waste liquor from sulphite mills contains from 12 to 20 per cent. of highly colored organic matter. In order to use this liquor in the textile industry as a finishing material or in the leather industry as a filling, it is necessary to decolorize it; according to *Paper* (8, 29), it has been found that phosphoric acid under certain conditions possesses the property of separating a red coloring substance from the liquor in an insoluble form; a recent German patent covers a process by which this is effected. To carry out the process, all the free acids stronger than phosphoric acid are first removed from the liquor: insoluble carbonates, such as calcium carbonate, are added, and the excess is removed by filtration. Such an amount of phosphoric acid is then added that about equal parts of liquor and acid are present. The mixture is concentrated, and the organic thio-compounds in the waste sulphite liquor are decomposed by the phosphoric acid; sulphurous acid separates, while the phosphoric acid combines with the lime present as "sulpholignate" to form an insoluble calcium phosphate which may be employed as a fertilizer. The separation of the red coloring matter occurs after the elimination of the sulphurous acid.

ITALIAN SHIPMENTS OF CARBON DISULPHIDE.

According to *The Chemical Engineer* (16, 41), a shipment of 50 tons of carbon disulphide has recently been made from Catania, Italy, to the United States. This shipment, it is learned, is the forerunner of a monthly consignment of like amount. This fact, coupled with several inquiries received from rubber manufacturers, induces the belief that a shortage in the supply of that product exists in the United States. When it is considered that there is a duty of 25 per cent. on the product, that owing to its highly inflammable nature difficulties are encountered in finding vessels which will carry it, that the freight is $18.25 per ton, that the containers (iron drums) are of two-thirds the value of the product and are subject to a duty of 45 per cent., it must be evident that the seeking of this product in a foreign market is hardly a matter of price, but is the result of inadequate production in the United States. There is one establishment producing carbon disulphide at Catania, a sulphur center, Sicily, namely, L'Insulare. It began operations some 12 years ago to supply a local demand, where the article is used in extracting the oil remaining in the residuum of olive oil presses.

THE CONDITION OF THE CHILEAN SALTPETER INDUSTRY.

According to *Die Chemische Industrie*, 35, No. 13, 420, in the period from May 1, 1911, to April 30, 1912, the world's saltpeter consignment was increased by 115,000 tons as compared with a similar period the past year. The total consignments for the year ending April, 30, 1912, were:

	Tons.
In Europe and Egypt	1,848,000
In the United States and remaining countries	550,000
Total consignments	2,398,000

In 1911, the total consignments were 2,285,000 tons, 1,661,000 tons of which went to Europe and Egypt.

The falling off in America is explained by the substitution of cotton-seed residue, much of which was on the market in 1911. This, however, is looked upon as a matter of passing importance. In the last four months, the Chilean production decreased 5,000 tons, owing to the scarcity of laborers and to the low price prevailing for saltpeter. There is also much competition in the saltpeter industry, while the ammonium sulphate industry is practically in one hand. It is stated that the nitrogen price varies 1.31 M. per kg. for saltpeter and 1.39 M. per kg. in the case of ammonium sulphate.

METHYL CHLORIDE AS A REFRIGERATING AGENT.

Methyl chloride has been used to some extent as a means of producing cold and its use has been suggested in refrigerating machines. It is non-poisonous, although anaesthetic, and by its evaporation a temperature of —23° C. is produced, while with air-blowing a temperature of —55° C. may be reached. A mixture of 88 per cent. air and 12 per cent. methyl chloride by volume is exploded only by electric sparks or a powder fuse, and not by flames; when the content of methyl chloride falls below 10 per cent. or is raised above 15 per cent., the mixture does not ignite (*Z. Ges. Schiess- u. Sprengstoffw.*, 6, 304). Lachmann and Heylandt Ges. m. b. H. (French Patent 438,727, 1912) now claim methyl fluoride either alone or mixed with other gases, as methyl chloride, for use as a refrigerating agent. Considerable quantities of methyl chloride are wasted in the chlorination of denatured spirit, and it may be prepared, if required in large quantities, by the chlorination of natural gas.

ACCELERATING PAINT DRYING WITH OZONIZED AIR.

A method of hastening the drying of paint, particularly freshly applied paint on automobile bodies, by means of ozone, has recently been tried out. The ozone was carried by forced draft into the drying room, where it came into contact with "green" paint on a newly painted body selected for the test. Another body, having an equal amount of paint spread over the same area, was placed in a natural atmosphere. At the end of an hour the body kept in the ozonized air had gained 1.67 per cent. in weight, while the other had increased only 1.13 per cent. At the end of a second hour the respective increases in weight were 3.34 per cent. and 1.51 per cent.; while after 15 hours the ozone-treated body had gained 19.74 per cent., as against a total increase of 9.76 per cent. for the other. The treatment with ozonized air thus showed an advantage of more than 100 per cent. over plain air drying.

A NEW PROCESS FOR PRODUCING STEARIC ACID.

Another process for the production of stearic acid from oleic acid is claimed in a recent German Patent (No. 247,454). According to the specification, oleic acid or its esters is treated with concentrated sulphuric acid, and the product, after washing free from sulphuric acid, is reduced to stearic acid by means of an electric current. In more detail, the process is as follows: The sulpho-acid is washed with cold water to free it from sulphuric acid, and is then dissolved in boiling water. The water solution thus obtained is made the catolyte in a diaphragm cell, a 30 per cent. sulphuric acid solution serving as the anolyte. Lead electrodes are employed, with a current density of from 2.5 to 10 amperes per sq. ft. After the passage of the current for about one-fifth of the time indicated theoretically—assuming 100 per cent. current efficiency—as required to complete the reduction, the fatty acids separate out and are again treated with sulphuric acid and electrolyzed. It is said that by repeating the operation several times, oleic acid may be almost quantitatively converted into stearic acid.

THE RAPID PRODUCTION OF PURE CREAM OF TARTAR.

In German Patent 247,452, recently issued, is described a simple means of obtaining cream of tartar of a high grade of purity by a single operation. The discovery was made that the

presence of chloride or nitrate of aluminum increases the solubility of potassium bitartrate in hot water while it decreases its solubility in cold water. Accordingly, the process has been patented wherein the raw material is extracted with a hot solution of an aluminum salt instead of with water, with the result, it is claimed, that a very large crop of crystals of at least 99 per cent. purity are recovered on the first crystallization. The presence of aluminum salts in the liquors is said to have the further advantage of arresting fermentation.

"DURIRON."

"Duriron" is a new acid, alkali and rust-proof metal for which there has been considerable demand as a material for acid-cocks, concentrating pans, stirrers, pipe and bowls. It possesses a density of 6.56, a melting-point of 2550° F., tensile strength of 15,000 pounds per sq. in., and a compression strength of 70,000 pounds per sq. in. It is harder than cast iron, and it must be ground and not machined. The manufacturers state that the following tests were made in cold reagents on rough samples, as taken from the sand:

	Percentage losses.		
Period of immersion.	24 hrs.	48 hrs.	72 hrs.
Sulphuric acid, conc.	none	none	none
Sulphuric acid, 10 per cent.	0.0142	0.0226	0.0309
Nitric acid, strong	0.0002	0.0004	0.0005
Nitric acid, 25 per cent.	0.0004	0.0007	0.0008
Hydrochloric acid, conc.	0.0338	0.0641	0.0922
Acetic acid	0.0002	0.0002	0.0003
Tartaric acid, 25 per cent.	0.0006	0.0012	0.0012
Chromic acid, 10 per cent.	0.0002	0.0003	0.0005
Oxalic acid, 25 per cent.	0.0013	.....	.....
Moist chlorine gas	0.0008	.....	.....
Ammonium chloride	none	0.0001	0.0002
Sodium chloride	none	none	none
Calcium chloride	none	none	none
Cyanide solution	none	none	none

LEAD FOR CALKING JOINTS.

Lead has been used for centuries to calk pipe joints, the process in vogue being to melt the lead, pour it into the joint, and then calk or hammer the lead to expand it. Recently two new forms of lead have been introduced in England for calking. "Ribbonite" lead, which is used for joint-calking, consists of shavings of lead twisted into the form of ropes, which are calked into water-pipe joints in the place of cast lead. Lead wool is also used for pipe joints and is now employed by many London gas companies; it was lately used in making the joints in $7\frac{1}{2}$ miles of water-piping at Staines, England. It is announced that an American company has brought out lead wool and rope for calking purposes (*Pop. Mech.*, **18**, 159). Lead rope is said to be made of especially refined metal, very finely stranded, each strand measuring 0.007 inch, and the rope $\frac{1}{2}$ inch in diameter. When hammered, this rope becomes very dense and no skill is said to be required to pack it into joints.

"VANALIUM."

"Vanalium" is an aluminum alloy, about 3 per cent. heavier than aluminum. It bears rolling into sheets and drawing into wire, and can be worked very much like brass. It takes a high polish and resembles aluminum in color. "Vanalium" is said to be unaffected by ordinary atmospheric conditions, and by hydrogen sulphide, carbonic acid, sulphurous acid and mineral waters. When cast, the metal has a tensile strength of over 11 tons per sq. in., a yield-point of 8 tons per sq. in., with an elongation of 8 per cent. in 2 in., and can be cast in either iron or sand moulds. By rolling, it is said that the strength is more than doubled, and by drawing, trebled. The alloy retains its hardness after being subjected to heat better than other aluminum alloys, and it melts at about 650° C. It is not affected by sea-water and can be readily soldered.

"ARGILITE."

This new alloy, the invention of G. Jacquier (*Mech. Eng.*, **29**, 757), is intended for the manufacture of pipes, tubes and armor plate. It contains 90 per cent. aluminum, 6 per cent. copper, 2 per cent. silicon, and 2 per cent. bismuth, and is said to be light, hard and to possess great resistance to pressure and corrosion.

A WATER FLOW RECORDER.

The Lea Water Flow Recorder, described in *The Engineering and Mining Journal* (**93**, No. 22, 1089), is said to show all irregularities in the boiler feed, to record the quantity of water evaporated per pound of coal, and to thus show the number of heat units in the coal.

The apparatus works on the V-notch weir principle and is described as follows: A float spindle passes through the bottom of the instrument case, gearing into a small pinion upon the axis of a drum revolving between centers. Upon the body of the drum is a screw thread, the contour of which is the curve of flow for the V-notch, in connection with which the recorder is used. The spiral drum serves a double purpose: Its screw thread rectifies the motion of the recording pen, so that it moves equal distances for equal increments in the rate of flow; it provides a magnified scale for making an accurate observation of the rate of flow at any moment.

The actual depth of water in the notch can always be observed, and the instantaneous rate of flow in pounds or gallons can be seen with accuracy. The recording pen which moves in direct proportion to the rate of flow produces a diagram, the area of which is a measure of the total quantity, and this can easily be deduced by means of a standard planimeter.

Heretofore, the Lea recorder was made on the open or atmospheric principle, but recently the manufacturers added a new type. The notched tank is made of cast iron, similar to the standard open-heater construction. The tank is entirely closed and is suitable for withstanding any pressure or vacuum up to 10 lb. The operating head of the Lea recorder is only about 18 in. and is made in sizes from 200 to 10,000 boiler-horsepower.

Besides being used for the measurement of boiler-feed water, steam consumption, etc., the Lea recorder can also be used for measuring pump discharges, flow of streams, acids, etc. For measuring the flow of acids the apparatus is provided with wooden tanks lined with lead, and the V-notch plate is similarly made. Hard lead or glass, however, can be used.

The apparatus is guaranteed to produce records which shall be within $1\frac{1}{2}$ per cent. of absolute accuracy by weight; also that the average error due to variations of temperature over a range of 50° F. (*i. e.*, 25° F. on either side of the normal) shall not exceed 0.5 per cent.

THE MANUFACTURE OF SUCTION HOSE.

The fabrication of suction hose is described in the *India-Rubber Journal*, **44**, 22, 73. This type of hose, generally used in connection with pumping operations of all kinds, is armored either inside or out, or both. In suction hose with a spiral wire inside, the canvas used should weigh from 12 to 16 oz. per yard and should be made of Egyptian or American cotton; the wire should be galvanized. For 2 inch suction hose, the following particulars are given:

	1 ply.	2 ply.	3 ply.	4 ply.	5 ply
Wire	12G	12	12	12	12
Inside rubber	17G	17	17	17	17
Width canvas	7 ½	14	21 ½	29 ¼	37
Outside rubber	23G	23	23	23	23

For suction hose up to $1\frac{1}{4}$ in. diameter it is usual to run the inside lining on to a mandril by a tubing machine; for larger sizes, it is considered advisable to build these up by hand in

the usual manner. For suction purposes, the spiral armoring wire is most satisfactory if put around the inside rubber lining, for it tends then to prevent the drawing-in of the canvas when pumping commences. For pressure hose, it is considered advisable to have the layer of canvas rolled on to the inside rubber coating, the wire armoring then being proceeded with on the top of this. There are three general forms of suction hose: round wire suction, flat wire suction, and internal wire suction. Some times the hose is bound with cord after the cloth wrapping is carried out. Outside armoring is advised only where there is rough usage.

HEAT TRANSMISSION IN VACUUM EVAPORATOR TUBES.

M'Cormack, Dormitzer and Roleson conducted a series of experiments to determine the efficiencies of a Swenson evaporator using tubes of four different materials, namely, copper, steel, lead and tin (*Chem. Eng.*, **16**, 1). Since it is known that slight variations in the composition of the metal exert considerable influence on the heat conductivity, the tubes tested were analyzed by standard methods. The results show that the efficiency is highest for the copper tubes and next highest for the steel tubes; this is as one would expect, as copper and steel possess a higher coefficient of heat transmission than the other materials used, and also owing to the fact that the copper and steel tubes used were from one-third to one-fourth as thick as the other two sets of tubes. Although the coefficient of heat transmission for tin is greater than that of lead, and although the lead tubes were about one-eighth thicker, the efficiency of the latter was found to be greater. In general, it may be said that there was found to be very little difference in the efficiencies for the various tubes, the maximum difference being 6.7 per cent. As the authors note, this is doubtless to be attributed to the fact that with tubes of this small thickness the coefficient of heat transmission does not materially effect the efficiency.

A NEW CRUDE OIL ENGINE.

The "Blackstone" semi-Diesel type of crude oil engine, described in *Gas and Oil Power*, **7**, 471, is said to be capable of working on all kinds of crude oils, both shale and petroleum, as well as upon petroleum residues, consuming the fuel without leaving any residue and this without the aid of an abnormally high compression. The fuel is injected into the cylinder by means of compressed air at 400 pounds, the main air compression in the cylinder being not more than 150 pounds. The fuel charge is ignited by a flame produced by the combustion of a small auxiliary charge of oil injected at every cycle into a bulb or igniter kept hot by the repeated combustions. The main cylinder fuel spray is regulated by the governor, and the engines run economically on any load. A feature of these engines is the prolonged injection of the main spray fuel, which maintains the initial pressure during a considerable portion of the working stroke, thus ensuring a maximum amount of power with a minimum of cylinder volume. This type of engine is made both stationary and portable, the stationary up to 300 B. h. p. Vertical multi-cylinder engines are also manufactured for marine purposes, driving dynamos, etc.

A DOUBLE-OILING SYSTEM PUMP.

The "Sterling" double-oiling system pump, described in *Power*, **36**, 103, is designed to handle clean and dirty oil at the same time. The main casting contains a steel rack plunger which is reciprocated by a gear segment fastened to a shaft extending through the pump and having at its outer end a lever connected to some moving part of the engine. The operating lever has eight adjusting holes to control the amount of oil pumped, and it is also adjustable on the shaft which it drives so that it may be set at any angle. It is therefore possible to arrange the movement of the main pumping plunger so that it will travel from its extreme position at the end of the stroke inwardly much or little and the pump may just comfortably handle the amount of dirty oil which it receives without drawing large quantities of air through the receiving well of the dirty-oil system. The driving rod connecting from the engine to the pump is $^3/_8$ in. pipe. The pump casting has a hollow portion in the top which acts as an air cushion or dome for the discharge of both ends and the steel ball valves at each end are accessible without disturbing any piping or removing their seats.

AIR-JET CHIMNEY VENTILATOR.

A Philadelphia firm is manufacturing a ventilator system in which the draft is created by an air-jet chimney ventilator, the operating air being produced by a rotary blower which creates a suction or negative pressure in the furnace. On the average, the blower consumes 0.5 per cent. of the fuel burned, and at the heaviest load of the grate 1 per cent. The combustion gases do not pass through the blower, so repairs and replacements are not expensive. The system is said to considerably increase the capacity, efficiency, and advantages of the superheater and economizer, as but a small quantity of gases of high temperature are utilized in them. With a varying steam consumption, it is claimed that one boiler may be forced for a time without putting extra boilers in operation, and, most important of all the advantages, it is possible to use low-grade fuels such as lignite, brown coal, etc., in the furnace.

THE UTILIZATION OF PEAT.

In 1907, the peat industry of Europe was investigated by the Department of Mines of Canada, and later a report was published in which the European practice was discussed in detail. In order to determine the possibilities of peat fuel for industrial purposes, the Department purchased some 300 acres of peat bog and has been experimenting with the foreign systems. In the manufacture of air-dried fuel from peat bogs, the peat has been dug by hand, transferred by an elevator into a mill, the resulting pulp conveyed by cable cars to the drying fields, rolled into a sheet about 4 in. thick by a press, and divided by knives into blocks which are then dried on the field. Allowing 140 days for a season's work, the cost of fuel on the field is said to be $1.40 a ton and when stored in the shed $1.65 per ton. In Sweden, the cost of a plant for the manufacture of 20,000 tons of peat powder by the Ekelund system is $86,000, and the cost of producing one ton is $2.30; in Canada, however, the cost per ton is higher, for common labor in Sweden gets a wage of but $1.00 to $1.22 per day of 10 hours. While peat powder has been found to be satisfactory as a fuel in Sweden, because of the expense of production, waste of available nitrogen, etc., Eugene Haanel, the Director of the Department of Mines of Canada, has concluded, after considerable experimentation, that the proper method is to gasify the peat in a suitable producer, along the lines of the ideas advocated by Frank and Caro, and also applied in Ziegler's peat gas-producer; and considers that in order to make the peat industry profitable, a 20 hour day, working 2 shifts, must be adopted, as the real season for working a Canadian bog is not over 110 working days a year.

Thackara (*The Gas Engine*, **14**, 318) states that the production of gas from peat having a water content up to 20 per cent. for use in suction gas engines has met with considerable success in Germany, but for a number of years efforts have been made to utilize peat with a water content as high as 50 to 60 per cent. and thus eliminate the expensive drying process. It is now found that peat containing 40 per cent. of water and costing $0.57 per metric ton, may be used with the Gorlitz engine, the consumption per kw.-hr. being 3.43 pounds for one trial and 5.31 pounds for another.

NOTES AND CORRESPONDENCE

SEAWEED, POTASH AND IODINE.

In THIS JOURNAL, Vol 4, No 8, page 623, which has just come to hand, there is a note by Hendrick Knudsen, entitled "Sea Weed, Potash and Iodine, A Criticism." The criticism is of a preliminary report prepared by myself, on work done last year under my direction and published as Senate Document 190, Sixty-second Congress, Second Session. The major part of the criticism is captious, indefinite, an expression of personal opinions and calls for no comment. Some of the statements, however, may prove not only misleading but quite mischievous. The author claims to be an expert with more than 20 years' experience. But Mr. Knudsen has not studied nor had any practical experience with the giant kelps of the Pacific Coast and totally misapprehends the conditions existing there in assuming that the methods formerly employed in Norway are applicable. Moreover, he is looking at the matter from the point of view of iodine production, while I was concerned with the possibility of utilizing the kelps as sources of potash. This is clearly evident from a reading of the present critique as it was in a plan for the investigation which Mr. Knudsen submitted for my consideration before the work was undertaken. I disagree absolutely with Mr. Knudsen's conclusion that potash from kelp can come only as a by-product of the iodine industry. Rather, so far as the Pacific kelps are concerned, iodine production is a possible side issue to a very probable potash industry.

It would appear from the critique that *Fucus* was given special consideration. This is not so, as it is discussed only incidentally in a general consideration of the algae. *Laminaria*, the species of especial importance as iodine gatherers, are not particularly prominent on the Pacific Coast, and there is no great promise that an iodine industry *per se* may be looked for there. As the Senate Document clearly shows, the important "potash" varieties are *Nereocystis leutkeana* in northern waters, and *Macrocystis pyrifera*, south of Point Sur. These occur in large beds or groves of practically pure stands. Drift kelp washed ashore is gathered and sold to some extent now, but is not, nor is ever likely to be, worthy of being designated as a commercial industry.[1] It is appreciably lower in potash content than the growing kelp.

Mr. Knudsen's labored calculations to prove that the stand of giant kelps is not sufficient to meet this country's potash requirements ignore the facts. About 1,250,000 tons of potassium salts are imported, varying in composition from 8 to 65 per cent. potash content but far more of the lower than of the high grades, so that the average composition corresponds to appreciably less than 25 per cent. potassium chloride. More than this quantity of potassium chloride, in kelp, is shown in the maps in Senate Document No. 190, and vastly more will be shown when our entire resources are mapped and estimated as will no doubt be done in due course of time. Even more wide from the mark are Mr. Knudsen's calculations of the cost of harvesting. If one man had to row out to the beds, cut and drag ashore and burn enough kelp to make a ton of ash, it might very well cost $22 and probably much more. It will not be done that way, however, and enough has already been done to show that with large scale mechanical devices, the cost of harvesting and drying the kelp should not be a tenth of what Mr. Knudsen estimates.

Knudsen's estimates of cost of production are absurdly wide of the mark. I cannot give any figures with a claim for accuracy, for there is not sufficient existing experience on which to base accurate calculations. From what I have seen done with an experimental plant, I estimate that at several points on the California coast the kelp can be cut, hauled ashore and dried at about 85 cents, and certainly less than $2, a dry ton. This dried kelp can be ground in a ball mill for less than 40 cents a ton. Besides containing organic matter, nitrogenous materials and appreciable amounts of phosphates, all with a value for fertilizer purposes, it will contain 25 per cent. or more of potassium chloride, worth more than 70 cents a unit as present prices go. Consequently I should revise Knudsen's estimates to the following:

Value per ton (2,000 lbs.) of dried kelp		$10.50
Cost of harvesting	$2.00	
Grinding	0.40	
Overhead charges	0.15	
Selling cost, etc.	0.10	
Depreciation	0.05	
	$2.70	2.70
Profit		$ 7.80

This estimate does not include the item of containers nor transportation charges. The real problem is whether the margin is sufficient to meet such charges to points of present demand for potash fertilizers. It is expected that the opening of the Panama Canal will answer this question.

This ton of dried kelp will contain about 6 pounds of iodine, worth (Knudsen's figures) $11.52. What it would cost to obtain this iodine cannot yet be estimated satisfactorily. Undoubtedly oil fuel and a retort would be used. It is inconceivable that the archaic kelp ash method assumed by Knudsen would receive any consideration on the Pacific coast. While disclaiming any accuracy for the following figures, I regard them as far more reasonable estimates than those of Mr. Knudsen:

Harvesting and drying per ton of dried kelp	$2.00	
Fuel	1.50	
Labor	0.45	
Chemicals	1.10	
Overhead charges	0.15	
Deterioration, interest, etc.	0.10	
Selling cost for potash	0.10	
Selling cost for iodine	0.50	
	$5.90	
800 lbs. salts, 60 per cent. KCl, at 75 cents per unit		$10.60
6 lbs. iodine, at $1.92 per pound		11.52
		$22.12
Expense		5.90
Profit		$16.22

Apparently it would pay better to recover the iodine but, as pointed out in Senate Document No. 190, the market does not exist for all that could be produced from kelp. Moreover, there is good reason to believe that the present price is an artificial one and that iodine from the mother liquors of Chile saltpeter could and possibly would be put on the American market at any figure at which iodine from kelp could be produced. Iodine from kelp, therefore, seems to be largely a question of finding increased uses for iodine, but potash from kelp seems to be a certainty, either when our western states come to use fertilizers or when reasonable transportation charges to the East have been established.

Whether or not it would be profitable to prepare from the kelp salts, potash salts of high purity, is still another question. It can undoubtedly be done since, technically, the problem is not any more, if as difficult, as the preparation of such salts from the Stassfurt materials. The labor and transportation factors

[1] There is a company on the Southern California Coast, whose process is to cut the kelp and market the chopped green product for direct application to the soil.

on the Pacific Coast are too uncertain as yet to justify any definite estimates, and opinions only are hardly worth offering.

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ORDINARY WRITING FLUID FOR MARKING PORCELAIN CRUCIBLES.

Editor of the Journal of Industrial and Engineering Chemistry:

In the article on "Marking Porcelain and Silica Crucibles, etc.," published on page 567 of the August issue of THIS JOURNAL, I note the author has experienced a great deal of difficulty in permanently marking glazed crucibles and also note that he has gone to considerable trouble to remedy this difficulty.

While I was employed as "helper" in the U. S. Food and Drug Inspection Laboratory, Portland, Oregon, the same trouble was experienced there, as it is no doubt in most laboratories. We had been marking the crucibles on the bottoms with a piece of magnetite or some other iron ore, but this was impractical, as each crucible had to be lifted up to read the number, so I tried the iron in the form of ordinary black writing fluid from my fountain pen, on the glazed side of the crucibles. The method is as follows:

The crucibles are washed and dried with a clean towel, the numbers put on with the pen and dried carefully so as not to make the outlines of the figures ragged, by holding them about a foot above the Bunsen burner. The ink is applied two or three times, drying after each application and holding in a position so that it will dry in a uniform mark. After the ink is well set, the crucible is held in the flame and heated for about two minutes after it has become red hot. This oxidizes the iron in the ink and burns it into the porcelain, thereby marking it with a beautiful reddish gold numeral which cannot come off. If difficulty is experienced in placing a neat numeral on the crucible it may be outlined in dots, which gives a very pretty effect.

This simple method furnishes a reagent which is always at hand and one that is inexpensive, quick to apply and permanent. After three years' use, marks made in this way show up as bright as when they were taken out of the flame.

Very respectfully,

CLAUDE D. MASON.

IDAHO STATE BOARD OF HEALTH,
BOISE, August 12, 1912.

THE NEED OF CHEMICAL CONTROL IN FURNACE OPERATION.

During the past year I have visited several hundred power plants in this section of the country and as a chemist have been particularly impressed with the lack of instruments for determining furnace efficiency, *i. e.*, automatic CO_2 recorders and continuous gas samplers for sampling flue gas over a period of a number of hours; even the familiar Orsat apparatus is notable by its absence. Furthermore, in 90 per cent. of the cases, in the few plants where something of the kind was found, the instruments had been consigned to the scrap heap or stored and were never used.

The reason seems to lie in the thought that with coal at $1.50 per ton the possible saving would not be worth while. But it has been conclusively proved that the use of these instruments will result, even in this low-priced fuel district, in saving both the cost of instruments and of operation many times over. The losses which take place in furnaces are the most glaring of modern plant operation, yet they receive the least attention.

To the chemists the cause for this is not far to seek. Combustion is essentially a chemical process and it is easier for him to comprehend the chances for loss than one not thoroughly versed in the science. Still more important is the fact that the determination of furnace efficiency involves analysis of the flue gases, a chemical process involving the handling of the delicate gas analysis apparatus, an operation requiring some little skill and more or less constant attention from day to day. This same skill, however, is not greater than necessitated by many other operations carried on daily by the stationary engineer. Why, then, is this not done? Simply because the man who has charge of the boiler room has not been trained in these lines as he has in others.

Right here lies the opportunity for the chemist, if there be one connected with the plant, to make a great saving in operating expenses, with a minimum amount of effort and time on his part. In those plants where I found furnace efficiency at the highest and the instruments for its determination in successful operation, this part of the work was in charge of the chemist. It took very little of his time for a reliable laboratory boy had been trained to do most of the work and make the necessary reports.

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THE ESTIMATION OF OXYGEN AND OCCLUDED GASES IN COPPER, ETC.—AUTHOR'S NOTE.

The methods of analysis given in my article under the above title (THIS JOURNAL, 4, 402), may be simplified by the following:

In the purification of Carbon Dioxide (p. 403), for tube (A), substitute: "A bulb tube of $CrO_3 + H_2SO_4$ (sp. gr. 1.84) heated by 1 foot of resistance wire wound over asbestos; then omit (D), the tube of dry chromous chloride."

In the purification of hydrogen (p. 403), for A, B and C, substitute the heated bulb tube of $CrO_3 + H_2SO_4$ described above.

If it is not convenient to use resistance wire for heating these bulbs, a lamp will answer the purpose.

GEORGE L. HEATH.

HUBBELL, MICH.

CHEMICAL INDUSTRIES OF NORWAY.

By Consul THOMAS H. NORTON.

Numerous factors have combined to retard the industrial progress of Norway. The climate is severe, coal is lacking, the mineral deposits are not easily accessible, the area of tillable land is very limited, and the industrial education of the people is not advanced.

Less than 3 per cent. of the land is under cultivation, about 25 per cent. is covered by forests, and the reminder consists essentially of moors, mountain pastures, lakes, and marshes. The conditions of life have been comparatively hard and emigration extensive. Exports to other countries have been limited chiefly to timber and the products of the extensive fisheries.

There is, however, now a marked change for the better. Norway bids fair to develop into an industrial state of considerable importance, and the chemical industries are the ones coming most prominently to the fore in the movement. The first step forward was taken in the development of the wood-pulp industry. The second, and most important for Norway's future, was the utilization of the country's magnificent water power for the establishment of electrotechnical and, more especially, of electrochemical industries on a scale impossible in any other European land.

The general movement forward in the manufacturing industries of the Kingdom, and more specifically in the various branches of applied chemistry, may be measured by the growth during the decade 1897–1908. It should be stated, in this connection, however, that a very noticeable increase in the establishment of new factories, mills, etc., began in 1890. It reached its maximum in 1899. There was a decline in the rate until 1904, when a new period of activity set in, and has continued uninterruptedly until the present time.

During the decade ending 1908, there was in Norwegian industry an increase of 45 per cent. in the number of "years of work" [illegible] the total number of days of work in a year divided by 300. This increase is five times greater than the increase of population. During the same period there was an increase of 150 per cent. in chemical manufacturing branches. There was an absolute increase of $21,440,000 in the amount of wages paid to operatives, representing an advance of 82 per cent. This advance in chemical industries amounted to 333 per cent.

The average annual wage for all operatives, in all industries, was $210.38 in 1897, in 1908 $264.52, an increase of 26 per cent. In chemical industries the average annual wage advanced 67 per cent. during the period. The average daily wage of adult operatives in all industries was $0.82 in 1900, and $0.92 in 1908.

Statistics of the Chemical and Allied Industries.—In 1897 there was, on an average, 1½ horse power employed per operative in Norwegian factories. In 1908 it had increased to 2½ horse power. The average establishment employed 45 horse power in 1897 and 76 in 1908.

Industries.	Factories.	Operatives.	Average daily wage.	Horse-power.
Chemical industries proper.				
Bone grinding	4	10	$.072	95
Calcium carbide	7	1,158	1.20	59,350
Chemicals:				
Heavy	13	429	0.94	729
Minor (ink, blacking, etc.)	19	80	0.61	61
Colors	8	66	0.84	108
Electrochemicals	9	675	1.18	40,045
Explosives	8	133	0.90	235
Fertilizers	13	132	0.69	638
Glue	2	57	0.76	142
Insulating material	3	11	1.36	12
Matches	5	918	0.73	464
Pharmaceutical products	10	52	0.60	23
Tar paper	2	8	0.72	...
Varnishes	3	12	0.79	.....
Total	106	3,741	.....	101,902
Candles, oils, power, etc.				
Candles	2	25	$0.47	8
Electric power, centrals	53	459	1.10	137,167
Gas works	6	57	1.00	34
Oils and by-products	17	376	0.88	896
Perfumes	1	6	0.77	.....
Petroleum:				
Briquetting	1	4	0.78	3
Refining	2	56	1.06	37
Soap	39	338	0.72	158
Steam power houses	3	5	1.01	367
Train oil:				
Refining	36	160	0.76	33
Rendering	15	87	0.80	73
Above combined	9	32	0.85	...
Total	184	1,605	....	138,777
Allied industries.				
Cement	1	160	$0.96	1,360
Copper smelting	4	232	1.00	1,100
Glass	9	1,143	0.84	214
Iron works	4	58	0.89	320
Mining of apatite, minerals, etc.	66	511	0.86	65
Ore mining	111	4,877	1.13	16,016
Paper	33	3,492	0.91	19,006
Tanneries	78	567	0.87	860
Treatment of minerals	6	168	0.73	531
Wood pulp:				
Chemical	23	4,563	1.00	27,307
Mechanical	66	3,475	0.94	108,188
Total	401	19,255	....	174,967
Grand total	691	24,601	....	415,646

The above table has been compiled to show the exact status of the Norwegian chemical industry in 1908, giving data on each separate branch. The classification of the Norwegian census is followed.

Importation of Heavy Chemicals.—In regard to most chemical products, Norway is still largely dependent upon other countries. Apart from her electrochemical industries, there is a fair development of the manufacture of matches, cellulose, fertilizers, oils, candles, iodine, and oxalic acids.

The heavy chemicals are imported chiefly from Germany and Great Britain. Sulphuric acid is manufactured cheaply, as the Norwegian pyrites is of excellent quality and is shipped in large quantities to other countries. The product of the three acid works in active operation is used chiefly for the manufacture of superphosphate and is inadequate to cover the needs of domestic industry. There is an annual import, valued at $42,000. Five small establishments furnish washing soda in crystals, but the main supply of soda ash, caustic soda, Glauber's salt, and bleaching powder is secured from Germany and elsewhere, as the country is dependent upon imported salt.

The utilization of kelp as a source of iodine and potash salts continues to be a prominent industry on the shores of Norway. As in the case of Scotland, Normandy and Japan, conditions seem to enable this time-honored branch still to maintain the competition with Chile iodine. In view of the exhaustion, within a measurable time, of the Chile nitrate deposits, it is well that the kelp industry is kept alive, and that studies are made to perfect its processes. There are nine establishments along the Norwegian coast occupied with this branch. Besides supplying the home demand, they exported in 1910 iodine to the value of $53,000 and 2,318 metric tons of kelp ash, valued at $64,000 (metric ton = 2,204.6 pounds). The current price of the latter is $27.34 per metric ton. Less is done in Norway than in Scotland to extract potash salts in a commercial form from this ash, although all of the kelp works furnish potash fertilizers. There is, however, a process in use for extracting from the kelp, before incineration, a highly mucilaginous substance that is a combination of potash with an acid present in seaweed. It is used to some extent in finishing textiles and is brought into commerce under the name of "norgine."

Manufacture of Oxalic Acid—Copper Pigments—Matches.—One large lumber firm at Frederiksstad carries on very successfully the manufacture of oxalic acid. It is made by fusing sawdust with a mixture of the caustic alkalies. Sodium oxalate is separated by crystallization from the solution of the fused product and transformed into calcium oxalate by treatment with milk of lime. The pure acid is secured from the calcium salt by the usual treatment with sulphuric acid. The export of oxalic acid, amounting to $37,000 in 1910, goes chiefly to the United States. The firm in question manufactures also such oxalates as are demanded in commerce.

The manufacture of copper pigments for use on the hulls of both wooden and steel vessels is highly developed in Norway, as is to be expected in a country possessing so extensive a mercantile marine. Nine establishments make a specialty of this product, and there is an annual export valued at $58,000.

Electrochemical Industries.—It is in the recent establishment of electrochemical industries upon a grand scale that Norway has disclosed her latent power as a coming factor in the field of applied chemistry. The vast, hitherto almost neglected water power is now being harnessed, one factory after another is coming into existence, and soon the Kingdom will present a remarkable exhibit of varied chemical industries, contributing largely to the world's markets and rapidly enriching the land.

This change began in 1899, when the first calcium carbide factory was built. The number of works has steadily increased until now there are seven in operation. In 1905 the first air-nitrate works began operation. Now a second on a much larger scale is about to open, and others are planned. In addition, there is a factory for cyanamide, one for sodium, one for aluminum, one for nickel, one for ferrosilicon, and one for electro steel. There are also several smaller experimental plants.

The products of these factories exported in 1910 had the following values: Calcium carbide, $1,627,000; calcium cyanamide, $184,000; calcium nitrate, $507,000; sodium nitrate, $58,000; sodium nitrite, $309,000; aluminum, $437,000; sodium, $63,000; ferrosilicon, $192,000; total, $3,377,000.

The exported products in the above categories were valued at $2,717,000 in 1909. The annual increase at present in the value of electrochemical products, as far as it can be measured by export statistics, is thus $660,000.

Manufacture of Calcium Carbide—Calcium Cyanamide.—The manufacture of calcium carbide was the pioneer electrical industry in Norway, and considerable English capital has been invested in this branch. A French company operates one plant at Hafslund. The Kellner Partington Paper Pulp Co., at Borregaard, is a good example of foreign investment in Norway. The company utilizes 24,000 horse power, and employs 3,000 workmen in its carbide factory, ferrosilicon works, and large pulp mill. It is the largest industrial establishment in the Kingdom. The Albion Products Co., at Notodden, and the Alby United Carbide Factories at Odda, are two other large English undertakings. At Trondhjem, the Meraker Carbide & Smelting Works have added to their extensive works plants for producing ferrochrome and ferrotitanium. The seven carbide works employ a total of 60,000 horse power. They are all located on the coast or on navigable rivers, and manufacture almost exclusively for exportation. In 1910 they shipped 50,579 metric tons at an average price of $32.16 per ton. The average daily yield per horse power is roughly estimated at $2^1/_3$ kilos, or 843 kilos in the year. In German factories the yield ranges from 3 to 5 kilos, as compared with a theoretical maximum of 8 kilos. The equipment of the carbide factories in Norway is essentially the same as that of the American factories.

An English company, the Northwestern Cyanamide Co., has built large works at Odda, on the Hardanger Fjord, and established on a successful basis the manufacture from atmospheric nitrogen of calcium cyanamide, which is competing with Norwegian calcium nitrate for recognition as the most economic form in which the air can furnish nitrogenous compounds for the needs of agriculture. The firm shipped 752 metric tons in 1909 and 4,281 tons in 1910. The price is $42.88 per metric ton. The industry is evidently on a firm footing and finds a market for its products, as do the similar works in Germany.

Air Nitrates—Sodium.—At Notodden, in 1905, the first factory for manufacturing nitric acid directly from the elementary gases of the atmosphere was erected. In an enlarged form it now gives occupation to 500 workmen, and is daily demonstrating the remarkable possibilities of this new factor in chemical industry and in economic evolution. The factory furnishes all the nitrates required for Norway in agriculture and the arts, and is shipping constantly increasing quantities to foreign countries. The exports for two years were as follows: 1909, calcium nitrate, 9,422 tons; sodium nitrite, 2,577 tons; sodium nitrite, 592 tons; 1910, calcium nitrate, 13,531 tons; sodium nitrite, 3,200 tons; sodium nitrate, 1,074 tons.

During 1911 the manufacture of ammonium nitrate for use in making explosives has been introduced upon a large scale, as it is profitable at present prices. Ammonia is imported from England, and after conversion into the nitrate is shipped back. A much larger factory is nearing completion at Saaheim and will be put in active operation before the close of 1911.

A single factory at Vadheim, on the west coast, is manufacturing sodium very successfully. The export in 1909 was 179 tons. The price is $0.536 per kilo, or $0.243 per pound. The process employed is that of the direct electrolysis of fused anhydrous caustic soda. Fusion vessels and cathode are of iron, and the anode is of nickel iron. The success of the operation depends largely upon the pains taken to keep the temperature of the bath within the narrow limits of 310° to 330° C. and the rapid removal from the cathode of the liberated metal. There is an increasing demand for sodium for use in making sodium cyanide, sodium amide, and especially sodium peroxide.

Production of Aluminum and Ferrosilicon. One large factory at Christianssand is devoted to the electrolytic production of aluminum. The process is practically identical with that employed in the large American works. The export of the metal was 486 metric tons in 1909 and 1,019 tons in 1910. This is equivalent to one-ninth of the annual American production. The Norwegain aluminum is sold at $0.43 per kilo. A considerable amount is employed in equipping the air-nitrate works, as the large conduits for acid gases and the pipings for nitric acid are all made of this metal.

The demand for ferrosilicon, so indispensable in the modern metallurgy of iron, is rapidly growing, as shown by the exports from both Norway and Sweden to other countries. In 1909 Norway shipped 2,645 metric tons abroad; in 1910 the export reached 5,121 tons. Much of the output is made in the electric furnaces at Borregaard.

Decreased Output of Nickel—Electrolytic Refining.—Norway possesses extensive deposits of nickel ores, much of it containing as high as 2 per cent. of the metal. In former years nickel mining was of some importance, but competition with the richer ores of Canada and the United States could not be maintained, and most of the mines ceased operation. During the closing decade of the last century the annual production of nickel sand amounted to 7 tons. Since 1900 the industry has revived, and there is an annual output now of 70 tons, nearly all of which is used in the Kingdom. In 1909 the only mine worked, that of Eije, yielded 5,770 tons of ore containing 1.1 per cent. of nickel. In the smelting works 2.77 tons of matte are obtained from 100 tons of ore. This matte contains 40 per cent. of nickel and 25 per cent. of copper. It is refined in the new electrolytic works at Christianssand, which are equipped for an annual production of 400 tons of the metal. The production of electrolytic nickel is a much more complicated operation than are those yielding aluminum or sodium. The copper-nickel matte is used as anode in a weak acid bath. Both metals are dissolved and pure copper is deposited on the cathode. At a certain point, when the electrolyte contains in solution a relatively large percentage of nickel, the current is interrupted. The remaining copper is first removed from the solution (by hydrogen sulphide) and then the iron is removed with the customary precipitants. From this purified and heated solution nickel is deposited electrolytically, insoluble anodes being used. The electrolytic nickel has a high degree of purity and is fairly compact. The total consumption of electricity is relatively large and the process can be employed with advantage only where the cost of the current is exceptionally low, as is the case in Norway.

Electric Smelting.—The success which has followed the experimental trials of the Gronwall furnace for the electric smelting of iron ores, first at Domnarfvet, in central Sweden, and later on a larger scale at Trollhattan, near Gothenburg (see Daily Consular and Trade Reports for May 6, July 19, and Oct. 14, 1911), has demonstrated beyond question the economic and technical advantages of this new process. The Norsk Electrometal Co. has promptly secured patent rights for Norway, and two companies are now constructing electric iron-smelting works under their licenses. The Hardanger Electriske, of Staalwerk, is erecting two furnaces at Odda that will use 5,800 horse power from the Tysse fall. The company controls in all 15,000 horse power at this point. At Arendal the Arendals Fosse-Compagni is building furnaces that will utilize 6,000 horse power, and is able to increase it to 30,000.

A somewhat different type of smelter is under construction near Notodden by the Tinfoss Jernoers Aktieselskab, which

will use at first 5,000 horse power and can increase it, if necessary, to 15,000. Unquestionably within a few months the electric manufacture of an excellent grade of iron will be established in Norway on a good working basis.

The electric smelting industry promises much for the country. In earlier years Norway possesses a flourishing iron industry, but saw it gradually decline as the fuel became more and more expensive. The land is rich in iron deposits, most of which are too remote to permit of advantageous mining at present. The Norwegian magnetite is not rich enough to warrant its export, and it is too hard for English smelters. If exported at all, it must usually be previously concentrated and briquetted, involving considerable expense. This magnetic iron ore, however, frequently contains sufficient lime to be self-fluxing. When adequate and cheap water power is near the mines, not only the magnetic ore, but the low-grade ores not worked at all now can easily be turned into first-class steel billets and offer a large margin of profit at present prices. It may be that Norway will rank eventually among the prominent iron-producing countries of Europe, as but little is known about the full extent of its mineral wealth, especially in the northern less-accessible regions.

Electric Steel Furnace.—Active steps are also being taken to introduce the electric steel furnace. The Hardanger Company is installing one requiring 800 horse power, and other plans are on foot. The fine grade of iron obtained by an electric smelter with the use of charcoal is almost free from manganese and silicon. If brought into a mixer heated with gas, and then refined in an electric furnace, the steel produced should be of an exceptional quality.

All of these plants and projects are dependent upon the continuance of the cheap rate for water power in Norway. In Sweden the cost per annual horsepower is apt to range above 50 crowns, or $13.40. In Norway, rates vary usually between $5.40 and $10.70. There are some cases where the cost is even as low as $4.

In addition to the foregoing enterprises, Norwegian capitalists are discussing the establishment of electric works for zinc smelting, for nickel smelting and for the combined electric smelting of copper ores and the electric refining of the metal.

Statistics of the Mines and Metallurgical Plants.—The following table shows the condition of the mines and metallurgical plants in 1909. Comparative figures of production for 1896 are added:

Ores.	Metric tons. 1896.	Metric tons. 1909.	Value in 1909.	Miners and operatives in 1909.
Apatite	1,485	1,364	$ 18,000	.....
Copper	36,956	42,612	450,000	2,243
Feldspar	15,568	36,489	127,000	.....
Gold	....	.....	2,000	47
Iron	6,510	40,389	79,000	681
Lead and zinc	452	983	6,000	262
Molybdenum	1	30	12,000	46
Nickel	422	5,770	27,000	78
Pyrites:				
Arsenical	.....	160	2,000	4
Iron and copper	87,867	282,806	1,638,000	1,867
Rutile	33	83	19,000	....
Silver	400	2,729	150,000	264
Metals smelted.				
Cobalt compounds	1	.....	.....	....
Copper	1,112	1,594	445,000	116
Nickel	7	70	29,000	57
Pig iron	366	.....	.....	....
Silver	4.8	7.8	134,000	11

In 1910 Norway purchased iron and steel to the amount of $4,581,000 and manufacturers of iron and steel valued at $4,832,000. Imports of other metals reached $1,397,000, and other metal manufactures, $6,243,000.

Striking Features of Norway's Chemical Industries.—In surveying the chemical industries of Norway there are several features worthy of careful study by the American economist. First and foremost is the systematic and exhaustive manner in which the abundant water power of the country is now being regulated, stored up, and pressed into service by the steadily increasing group of electrochemical industries. The best talent in the nation is enlisted in this cause, and the way is rapidly being opened for Norway to assume an industrial position commensurate with its geographical size and admirable facilities for maritime transportation.

In another field Norway has shown her ability to develop an industry, fitting in well with her enormous lumber interests, and that is in the manufacture of oxalic acid. It is a source of wonder that no attempt has yet been made to organize this branch of manufacture in the vicinity of some of the great American lumber centers, where sawdust, the primary raw material, is without value except as fuel. The United States buys annually oxalic acid from Norway to the value of $43,000, and from Germany to the value of $65,000. The American market should not be dependent upon European manufacturers for a chemical, the preparation of which is so comparatively simple.

As a market for American chemicals, Norway offers less of a field than the neighboring Scandinavian States, on account of the limited extent to which many industries consuming such products are developed at present. The character of the demand is much the same as in Denmark and Sweden. The quantity is relatively less.

CEMENT PRODUCTION AND TRADE OF THE FAR EAST.

According to Consul General George E. Anderson, of Hongkong, the cement industry of Hongkong and vicinity, which is the enterprise of one corporation but includes works in various portions of the colony and at Macao and Canton as well, has long dominated the cement trade of Southeast Asia and at times has had a not unimportant share in the import cement trade of the Pacific coast of the United States.

At the last general meeting of this company attention was called to the growing competition in cement making in the far East. In the course of his discussion of the situation the presiding officer at the company meeting said:

"Competition continues unabated but has somewhat changed in form. European shipments to the far East have decreased and in the main can be ignored. The establishment of new factories in near-by territory is what interferes with us most, and some of these are gradually improving the quality of their product and increasing their output. There are probably more factories in the East than the average man realizes; for, besides, the numerous Japanese establishments, including Manchurian, we have those at Tongshan (Tientsin), in Hupeh on the Yangtze at Haifong, at Kuala Lumpur, and a new one at Padang in Sumatra, and there may some day be one at Manila. To offset the rise of these establishments we have the ever-increasing call for cement. And if this increase continues in years of stagnation and troubled trade such as we have experienced lately, what may it be when China settles to a steady course and the inevitable railway building comes into full swing?"

No mention was made of the plant under the control of the Chinese Government at Canton, which is not in operation for the time being. The chief competition for Hongkong at present is coming from Haifong. The Manila enterprise referred to is under the control of a Philippine corporation organized for the purpose and is reported as well under way.

The total ordinary maximum output of the plants mentioned, which are now serving to a great extent much of China, particularly south of the Yangtze, the Philippines, Indo-China, the Malay States, and Siam, as well as other countries in lesser degree, probably aggregates more than 2,000,000 barrels annually. The maximum output, according to the best informa-

tion available, consists of the following, in barrels of 375 pounds each:

	Barrels
Green Island Cement Co. (Hongkong)	780,000
Ciments P. A. de l'Indo-Chine (Haifong)	300,000
Chee-Hsin Cement Co. (Tongshan, Tientsin)	300,000
Hupeh Cement Co.	288,000
Others	300,000
Maximum output	2,028,000

Competition with each other has prevented any one of the establishments concerned in this eastern trade from running at maximum capacity, and this is likely to be the case for sometime in the future. But, while competition has been and is likely to continue to be exceedingly keen, there appears to be no sound reason why all these plants shall not remain in the field. Each of these has more or less difficulties to overcome, but each has notable advantage either in the way of convenient and abundant supplies or unusually good shipping facilities, and all have cheap labor, fuel, and other supplies, and a constantly increasing demand for their product.

It seems quite likely, therefore, that the prospective increased demand for cement in China will be met with a complete and satisfactory supply in or near China.

Consul Stuart K. Lupton, of Karachi, India, states that the cement trade of northwestern India is comparatively small, as may be seen from the accompanying table of imports for the past five years, which means practically the entire consumption in a district with a population of some 45,000,000 people:

Year.	Casks.	Value.
1906–7	15,591	$38,126
1907–8	20,107	51,934
1908–9	22,729	59,181
1909–10	36,497	83,390
1910–11	33,095	75,579

Most of the cement imported is of British manufacture. The brands chiefly used are Victor, Rhinoceros, Gillingham, Peters, Elephant, Red Cross, and Pyramid among the English marks, with Gladiator as the principal German brand.

British cement is quoted by the manufacturers for March 23rd at $1.95 per cask, c. i. f. Karachi, and after paying a duty and handling charges is sold in smaller quantities to the consumer at $2.09 to $2.13 per cask. As freight rates from Great Britain are 20 to 25 shillings ($4.87 to $6.08) per ton, this means that cement must be produced at the shipping point for 50 or 60 cents a cask to realize a profit.

At the present time the Port Trust and the Karachi municipality are using about 1,200 casks of 400 pounds each every month; but this extraordinary work will soon close, and I am credibly informed that the average monthly consumption of cement for all purposes will be about 200 casks for the next eight months or a year.

SULPHUR, PYRITE, AND SULPHURIC ACID.

Mineral Resources of the United States, issued by the Geological Survey, states that the production of sulphur in the United States in 1911 amounted to 265,664 long tons, valued at $4,787,049, as compared with 255,534 tons, valued at $4,605,112, in 1910. In determining the value of most of the sulphur produced in 1911 the current market prices in New York were taken, from which the value at the mine was then computed. It is estimated that the production for the year 1911 is very close to the present rate of consumption.

Prices remained fairly constant throughout the year at approximately $22 per long ton at New York for prime Louisiana sulphur, and at $22.50 at Boston, Philadelphia, and Baltimore. Quotations on roll sulphur were from $1.85 to $2.15 per 100 pounds; for flowers of sulphur the range was from $2 to $2.40 per 100 pounds; and for sublimed sulphur it was from $2.20 to $2.60 per 100 pounds. Sicilian sulphur was held at the same figure.

In 1911 there were imported for consumption into the United States 29,144 long tons of sulphur, including crude, refined, flowers of sulphur, and other kinds. This sulphur was valued at $552,836. In 1910 the imports amounted to 30,833 long tons valued at $558,611. The great bulk of the sulphur imported comes from Japan.

In 1909 the United States exported 37,142 long tons of sulphur, valued at $736,928; in 1910 the exportation amounted to 30,742 tons, valued at $552,941; in 1911 the exports totaled 28,103 tons, worth $545,420.

The production of pyrite in the United States in 1911 amounted to 299,904 long tons, valued at $1,162,261. This was an increase in quantity of 58,292 long tons and in value of $184,283, as compared with the production of 1910. The figures are also the maximum ever recorded by the survey for the pyrite industry. Though low-grade sulphide ores of copper containing considerable quantities of pyrite and pyrrhotite and zinc sulphide concentrates have been used in recent years in the manufacture of sulphuric acid, this condition of affairs does not seem to have curtailed the output of pyrite, as it was feared it might. As a matter of fact, the output of pyrite has shown a great increased ring the last five years, notwithstanding this was a period of rapid development by the by-product sulphuric-acid industry. It is estimated that the quantity of sulphides other than straight pyrite used in the manufacture of sulphuric acid in 1911 was equivalent to 200,000 long tons of pyrite, which would bring the tonnage of this mineral theoretically produced in 1911 up to nearly 500,000 long tons. This does not include copper-bearing Spanish pyrite used in making sulphuric acid.

The importation of pyrite still greatly exceeds the domestic supply, as appears from the following statement of imports for consumption for the last three years: 1909, 688,843 long tons, value $2,428,580; 1910, 803,551 tons, value $2,748,647; 1911, 1,006,310 tons, value $3,788,803.

For the first time in the history of the volume, *Mineral Resources*, published by the Geological Survey, a brief statistical statement is made by the sulphuric-acid industry. One of the reasons for adding the subject of sulphuric acid is that, owing to the fact that so large a percentage of the output of sulphur and pyrite is converted into acid for use in the industries, the acid production becomes in a way a check on the statistics of sulphur and pyrite, especially of pyrite, which is practically all used in the acid industry.

The 1911 production of sulphuric acid in the United States aggregated 2,210,330 short tons, valued at $17,369,871, as follows: 50° Baumé, 1,026,896 tons, value $5,447,958; 60° Baumé 421,165 tons, value $2,624,042; 66° Baumé, 751,541 tons, value $9,176,297; other grades, 10,728 tons, value $121,575.

CHEMICAL INDUSTRY OF GERMANY.

Consul General A. M. Thackara, of Berlin, reports that with but few exceptions, conditions in the various branches of the German chemical industry during the year 1911 were most favorable. Heavy orders were received both for home and foreign consumption, and in many lines the prices for natural and artificial preparations were higher. The demands for drugs and chemicals were so large that the manufacturers of raw materials, such as acids, ammonia, etc., experienced great difficulty in filling their orders. There were especially notable increases in the demands for medicinal preparations on account of the numerous cases of illness, such as influenza, scarlet fever, diphtheria, and other ailments due to the heat of last summer. Many orders were received by the German manufacturers for disinfecting and other materials which were used in stamping out the plague in the far East.

Luftsaltpeter or air saltpeter manufactured from nitrogen ex-

tracted from the air by the Norwegian and Swedish plants is slowly finding its way to the market. It is expected that, in the near future, the Norwegian saltpeter can be shipped in large quantities to the centers of consumption. Its success as a competitor with the Chile product will naturally depend upon the price. At present the artificial saltpeter is selling at 8 to 9 pfennigs (1.9 to 2.1 cents) more per kilo (2.2 pounds) than Chile saltpeter, but it is thought that the prices will soon be equalized. In 1911 there were only 193.3 metric tons of soda saltpeter (natron saltpeter) imported from Norway, as against 730,939 tons received from Chile. In 1911 there were also imported 473.4 tons of nitrate of ammonia from Norway and 139.2 tons from Sweden, and 14,494 tons of nitrate of lime (Saltpetersäures Kalk) from Norway and 1,033.6 tons from Sweden. Not only in Sweden and Norway are new plants in course of construction for extracting nitrogen from the air, but also in Upper Bavaria, in the Tyrol, in Switzerland, and in the Valley of the Rhine.

The favorable business year of the German chemical industry is reflected in the increased dividends declared by many of the chemical companies, in the amount of capital invested in new companies, and in the capital used in extending existing industries. The total amount of new capital invested in the chemical industry last year was $16,226,840, compared with $6,333,180 for 1910. For last year $10,010,280 was employed for the creation of new companies and $6,216,560 for the extension of existing industries.

The drought of last summer unfavorably affected the crops of medicinal roots, leaves, and seeds, in consequence of which the prices of these raw materials were much higher. The prices of certain bulky products used in the chemical industry were also affected, owing to the difficulty of securing water transportation.

GERMAN POTASH AND SALT STATISTICS.

Consular Assistant Louis G. Dreyfus, Jr., of Berlin, reports that statistics recently published by the Ministry of the Interior giving the production of potash and salt mines in Germany, show that in 1910 there were 82 works, employing 27,790 persons, to whom was paid $8,869,678 in salaries and wages. Each of these figures was an advance over 1909, the record for that year being 78 works, 27,445 employees, and $8,400,077 paid in salaries and wages. Below is summarized the production for these two years.

Potash and salts.	1909. Metric tons.	1909. Value.	1910. Metric tons.	1910. Value.
Raw salts:				
Rock salt	1,103,562	$ 1,296,045	1,136,776	$ 1,344,269
Potash salts:				
Carnallite, inclusing kieserite	3,502,658	7,541,709	3,729,409	7,644,105
Kainite, sylvanite (sylvite)	3,570,286	11,508,021	4,610,152	13,862,702
Boracite	144	5,587	166	6,704
Salts to be used in further manufacture:				
Carnallite	3,353,993	7,262,482	3,569,937	7,382,753
Kainite, sylvanite	926,556	2,873,156	1,329,523	3,808,893
Products ready for sale:				
Stone salt	1,097,491	1,312,191	1,112,562	1,346,673
Carnallite with 9 to 12 per cent. K_2O	328,386	734,627	402,476	908,250
Crude salt with 12 to 15 per cent. K_2O	2,594,179	8,386,873	2,924,709	8,756,404
Salt with 15 to 19 per cent. K_2O	33,543	151,088	153,297	437,472
Fertilizer salts:				
With 20 to 22 per cent. K_2O	84,585	610,868	136,233	850,184
With 30 to 32 per cent. K_2O	43,713	505,370	55,556	626,330
With 40 to 42 per cent. K_2O	265,706	4,214,486	335,671	5,196,046
Potassium chloride:				
With 50 to 60 per cent. K_2O	266,911	8,295,233	304,145	8,673,969
With over 60 per cent. K_2O	107,537	3,662,667	130,767	4,336,013
Potassium sulphate of over 42 per cent. K_2O	69,730	2,608,336	90,389	3,239,079
Potassium magnesium sulphate	40,105	729,654	39,011	688,366
Magnesium sulphate	65,771	217,908	68,862	224,623
Magnesium chloride	28,983	84,848	31,012	92,911
Sodium bisulphite	4,445	34,452	2,540	19,078
Boracite	102	3,990	135	5,412
Bromine, etc.	11,390	501,623	14,293	472,496
Total	17,499,776	62,541,214	20,177,621	69,922,723

Among numerous references to the German potash industry that have appeared in Consular and Trade Reports were the articles published on Sept. 18, 1909; June 15, Aug. 30, Nov. 25, and December 12, 1910; Jan. 26, July 25, and Nov. 11, 1911.

THE WIDE USE OF ARSENIC.

The production of white arsenic in the United States in 1911 was 3,132 tons, valued at $73,408, against 1,497 tons, valued at $52,305, in 1910, according to a report on arsenic by Frank L. Hess, just issued by the United States Geological Survey. The arsenic was obtained as a by product of smelting operations. This output is much the largest ever made in this country, but owing to the low price and the distance of the smelters from New York, the freight charges absorbed a large proportion of the profit.

During the year 4,996 tons of white arsenic, metallic arsenic, and arsenic sulphides, valued at $247,323, were imported. Of this amount 1,921 tons was white arsenic, with a value of $116,948. In addition, 126,191 pounds of Paris green and London purple, valued at $4,972, were imported. The total production and importation in 1911 of arsenic and all arsenic compounds amounted to 16,256,000 pounds.

The principal uses of arsenic are in glass making, in pigments, and in insecticides. The use of Paris green (acetoarsenite of copper) in paint is somewhat limited on account of its poisonous quality. As an insecticide it is used largely by gardeners, orchardists, and farmers. If pure, it is comparatively harmless to plant life, owing to its insolubility, but the trioxide is often present in some quantity and if Paris green is then used it is fatal to plants, especially in dry climates, where it is not soon washed off by rains. Experiments conducted by a number of the State Agricultural experiment stations have demonstrated the value of arsenic when combined with lime as an effective spray against insect pests.

A number of arsenic salts and oxides are used medicinally, among them the bromide, iodide, trisulphide, trioxide, sodium arsenate, and potassium arsenate. Disulphide of arsenic, both natural and artificial, is used as a paint pigment; in calico printing and dyeing; in tanning; and, as it burns with an in-

tense white light, in fireworks. Orpiment, the trisulphide, called also king's yellow, is used as a paint pigment and as a reducing agent in chemical work. The trioxide is used in paints; for preserving hides, both for taxidermists and in the leather industry; as an antiseptic; and in killing animal pests. Sodium arsenate is used in dyeing with turkey-red oil and in printing fabrics; the arsenite in making soaps for use on skins and hides. Potassium arsenite is used as a reducer for silver in the manufacture of mirrors.

A copy of the report on arsenic may be obtained free on application to the Director of the United States Geological Survey at Washington, D. C.

SWISS FACTORY STATISTICS.

The following statistics, reported by Commercial Agent Archibald J. Wolfe, show the preliminary results of the Swiss Federal census of 1911 regarding Swiss factory enterprises:

Trades.	Factories.	Employees.		
		Male.	Female.	Total.
Cotton trades	326	11,617	17,932	29,549
Silk industry	215	7,735	23,802	31,537
Woolen industry	67	2,190	3,135	5,325
Linen industry	24	440	567	1,007
Embroidery	866	11,787	16,822	28,609
Other textile trades	112	1,517	2,633	4,150
Clothing and outfitting	660	8,789	16,061	24,850
Provisions and alimentary trades	694	13,440	12,604	26,044
Chemical industry	198	6,967	1,725	8,692
Centrals for power, gas, and water	263	4,254	1	4,255
Paper and graphic trades	625	13,227	4,930	18,157
Woodworking trades	1,268	23,333	432	23,765
Metal working	623	21,865	1,460	23,325
Machinery, apparatus, etc	640	45,313	1,122	46,435
Jewelry and watchmaking	856	21,445	13,538	34,983
Clay and stone trades	441	17,160	1,000	18,160

TITANIUM AND ALLOYS OF STEEL.

Much experimenting with various alloys of steel has been carried on by railroads and rolling-mill operators to produce a rail that will give more satisfactory service than the ordinary rail now in use. One of the principal metals used in these experiments, according to the United States Geological Survey, is titanium. More than 250,000 long tons of rails were rolled in 1910 from steel to which ferrotitanium had been added. More than 150,000 tons of steel rails in which nickel or nickel and chromium were used as alloy were also made during 1910, and experiments were made with about 80,000 tons of steel rails in which chromium, manganese, vanadium, and other metals were used. Certain steel makers, according to the Survey, are now advertising titanium steel, claiming that although no titanium is left in the steel, the removal of gases and impurities effected by it greatly increases the good quality of the steel.

GOOD INCREASE IN PLATINUM PRODUCTION.

California and Oregon produced all the platinum mined in the United States in 1911; this, as shown by Waldemar Lindgren, of the United States Geological Survey, in an advance chapter from "Mineral Resources" for 1911, was $8,631 greater in value than the output for 1910. The following is a statement of production in Troy ounces and the values for the two years:

	1910.		1911.	
	Ounces.	Value.	Ounces.	Value.
California	337	$8,386	511	$14,873
Oregon	53	1,121	117	3,265
	390	9,507	628	18,138

The average price paid for platinum in 1911 was $28.87 an ounce, compared with $24.38 in 1910, the higher price undoubtedly resulting in an increased production.

Importations in 1911 of crude platinum sands resulted in an estimated refined product of 27,500 ounces, nearly four times the domestic production. An additional amount was derived from imported ores and mattes, so that the total quantity of refined platinum produced in domestic refineries is estimated by Mr. Lindgren at approximately 29,140 fine ounces, of which about 940 ounces, valued at $40,890, was derived from domestic sources of various kinds—platinum sands, copper and gold bullion, etc. The corresponding estimate for 1910 was 773 ounces, valued at $25,277.

The platinum imported and entered for consumption in the United States in 1911, including ores and manufactured products, was valued at $4,866,207, an increase over the 1910 figures of $1,212,543. The exports amounted to only $8,139.

The world's production of platinum in 1911 was 314,323 troy ounces, compared with 288,952 ounces in 1910.

Mr. Lindgren's report of platinum contains an interesting discussion of the platinum-bearing minerals, the uses of the metal, its sources in the United States, and the possibility of new discoveries. It also contains notes on the other platinum metals such as iridium and palladium.

PAINT PRODUCTION IN 1911.

In 1911, according to the United States Geological Survey, the value of the paint produced from all sources was $31,822,827. Paints are divided by the Survey into three groups—natural mineral pigments, pigments made directly from ores, and chemically manufactured pigments. Of the total production of paint in 1911 $498,821 is to be credited to natural mineral pigments, $7,343,762 to pigments made directly from ores, and $23,780,244 to chemically manufactured pigments. The production of natural pigments was less than in 1910; that of pigments made from ores increased; that of chemically manufactured pigments decreased. There was a total decrease in value, compared with the value for 1910, of $241,495.

The report on mineral paints, by W. C. Phalen, of the Survey, has been issued as an advance chapter of the volume "Mineral Resources" for 1911. It contains tables showing imports of the pigments of different classes, thus giving an idea of the magnitude of their consumption in the United States; descriptions of the characters of the natural mineral pigments, and brief data on the methods of preparation of the prepared pigments. The report also contains a summary of the results of paint tests recently published by the American Society for Testing Materials.

WASTE IN COKE MAKING.

If the 27,703,644 short tons of coke manufactured in 1911 in ovens of the beehive type had been made in by-product ovens the value of the by-products thus recovered, which were wasted in the beehive ovens, would have been between $35,000,000 and $40,000,000. This interesting statement is made by Edward W. Parker, of the United States Geological Survey, in an advance chapter on coke from the volume "Mineral Resources" for 1911. This estimate is based on the value of the by-products resulting from the 7,847,845 tons of coke made in by-product ovens in 1911. The value of these by-products recovered in 1911 was equal to the value at the mines of the coal used in making the coke.

From information received by the Survey from the superintendent of motive power of the Pennsylvania Railroad Company, Mr. Parker estimates that the quantity of power which might be obtained from the coking operations in the Connellsville and Lower Connellsville districts by substituting non-recovery retort ovens for beehive ovens and using the heat which is now wasted would be more than twice the quantity of power necessary to move every train on the Pennsylvania Railroad between Pittsburgh and Harrisburg. The amount of boiler horse-

power obtainable from these coking districts is estimated by Mr. Parker at about 300,000 horsepower per hour for every day in the year.

COAL EXPORTS IN 1911.

The exports of coal from the United States during 1911, according to the United States Geological Survey, were 17,432,753 long tons, valued at $52,593,274, compared with 13,805,860 long tons, valued at $41,470,792, in 1910. The exports in 1911 comprised 3,553,999 long tons of anthracite, valued at $18,093,285, and 13,878,754 long tons of bituminous coal, valued at $34,499,989. The exports of bituminous coal increased over 3,000,000 tons, or about 30 per cent. Anthracite exports increased about half a million tons.

The imports of anthracite amounted in 1911 to only 2,463 long tons, valued at $12,550, and those of bituminous coal decreased from 1,497,709 long tons, valued at $3,975,561, in 1910, to 1,234,098 tons, valued at $3,604,797.

BOOK REVIEWS

CORRECTION.

Review of Thorpe's Dictionary of Applied Chemistry. Vol. I. THIS JOURNAL, 4, 550.

The price of $50.00 quoted in our review for the 5 volumes of the above work was a mistake. The price given by the publishers, Longmans, Green & Co., for the complete set of the second edition of this dictionary is $67.50.

A Dictionary of Applied Chemistry. Second Edition. By SIR EDWARD THORPE and other eminent contributors. To be issued in five volumes. Revised and enlarged, Volume II., 786 pages. Price, when complete, $67.50 per set and $13.50 per volume. Longmans, Green & Co. 1912, London and New York.

The issue of the first volume, reviewed in THIS JOURNAL, July, p. 550, has been followed with gratifying promptness by Volume II. This completes the treatment of subjects in alphabetical order up to and through Gold. A large number of new names has been added to the list of special contributors to this work and the same general policy of treating each subject by well known experts has been followed.

A comparison with the individual subjects treated in the first edition shows careful revision and enlargement of many articles. For example, the treatment of Chlorine has been enlarged to include the electrolytic production of this now important industrial product and includes reference to the commerical production of liquid chlorine.

New chapters have been added on Chromophores and Chromogens; Coke and its by-products and appliances used; Colloids; Condensers, laboratory; Corrosion of Iron; Crops; Desiccation and Drying; Diazo Compounds; Diffusion; Edible Oils and Fats; Egg; Esterification; Factis; Feeding Stuffs; Fertilizers and Manures; Fire Extinction and Prevention; Flame; Frits and Glazes.

The additions of new material together with the revision and modernizing of the chapters carried over from the previous edition bring this volume up to the high standard set by Volume I in both material and workmanship. M. C. WHITAKER.

Portland Cement. By RICHARD K. MEADE. Second Edition. 8vo. Pages viii + 385; 100 illustrations. Easton, Pa.: Chemical Publishing Co. 1911. Price, $3.50.

This excellent treatise, which was much sought after in the first edition, has been greatly improved in the second. The classification of cements is good, as is also the historical review, particularly that dealing with the development of the industry in America. The theories of composition are prudently dealt with mostly in the language of the chief investigators, such as Le Chatelier, Newberry, Richardson, Törnebohm and Day and Shepherd, who are all given the full credit due them. The chapter on raw materials is one of the best on that subject in any language. That on proportioning could well be cut down. The descriptions of the stages of manufacture are replete with detail. The review of the development of kilns, grinders and general mechanical appliances leaves nothing to be desired, at least as regards American practice. The author is strangely brief in speaking of the Universal Company's manufacture from slag and limestone. This is hardly fair, since such an enormous proportion of our American output is now made thus. The latter half of the book is taken up with treatises on analysis and physical testing of cement. In volume-constancy tests all are mentioned except high pressure steam tests.

This work on Portland Cement will always remain a monument to the industry and ability of the author. It is a pity that such flimsy paper should have been used in the embodiment of it.

CHARLES F. MCKENNA.

The Cement Industry in 1911. Published as an advance chapter from Mineral Resources, 1911, and may be obtained free by application to the Director, U. S. Geological Survey, Washington, D. C.

The statistics of cement production in 1911, prepared by Ernest F. Burchard, of the United States Geological Survey, show an increase over 1910 of only about a million and a half barrels. The increase in quantity is the smallest recorded within the last 13 years.

The total quantity of Portland, natural, and puzzolan cements produced in the United States during 1911 was 79,547,958 barrels, valued at $66,705,136. The year 1911 showed an increase of 2.27 per cent. in quantity, but a decrease of 1.48 per cent. in value.

The total production of Portland cement in the United States in 1911 as reported to the United States Geological Survey was 78,528,637 barrels, valued at $66,248,817.

This output represents an increase in quantity of 2.58 per cent. and a decrease in value of 2.87 per cent.

The United States has been divided into 11 subdivisions based on the grouping of plants in direct relation to the trade territory covered by each group. This grouping is also logical when the raw materials are considered.

PRODUCTION OF PORTLAND CEMENT IN 1911 BY COMMERCIAL DISTRICTS.

District.	Active plants.	Production 1911. Barrels.	Per cent. change, 1911.	Average factory price per bbl.
New Jersey and Eastern Pennsylvania (Lehigh District)	24	25,972,108	— 1.30	0.715
New York	7	3,314,217	+ 0.54	0.805
Ohio and Western Pennsylvania	9	6,756,313	+11.25	0.766
Michigan and Northeastern Indiana	13	4,519,726	— 0.11	0.827
Kentucky and Southern Indiana	3	2,818,820	— 0.21	0.793
Illinois and Northwestern Indiana	6	8,617,341	+ 2.88	0.791
Southeastern States (Maryland, Virginia, West Virginia, Tennessee, Georgia and Alabama)	11	4,049,063	+31.85	0.793
Iowa and Missouri	7	6,067,449	+ 6.02	0.862
Great Plains States (Kansas, Oklahoma and Central Texas)	17	7,010,396	— 9.23	0.834
Rocky Mountain States (Colorado, Utah, Montana, Arizona and Western Texas)	7	2,124,930	— 4.99	1.186
Pacific Coast States (California and Washington)	11	7,278,274	+13.98	1.406
Total	115	78,528,637	+ 2.58	0.844

Lehigh district produces eighteen million dollars worth.

The Lehigh District of Eastern Pennsylvania-New Jersey has, with three exceptions, shown a steady increase in production each year from 1890 to the present time. The years in which slight decreases are recorded are 1893, 1908, and 1911. The first two decreases were coincident with years of general business depression, but the decrease in 1911 may perhaps be in large part attributed to an over-production in 1910. The production for 1911 was 25,972,108, valued at $18,568,670, or 71.5 cents per barrel. This production represented a decrease in quantity of 343,251 barrels, and in value of $619,845 as compared with the production of 1910, an average decrease in price of 1.4 cents a barrel. There was no net gain or loss in the number of producing plants in the Lehigh district, but the starting of new plants in the South and West resulted in lowering once more the Lehigh district's proportion of the total output of cement in the United States.

The year opened with the prices on the downward grade, and there were only temporary revivals. Taken as a whole and judged by the personal testimony of representative cement manufacturers from all States east of the Rocky Mountains, prices appear to have been very unsatisfactory.

In 1911, 115 plants reported a production of Portland cement as compared with 111 plants in 1910. The total number of rotary kilns in the producing plants was 916 as compared with 902 in 1910. These kilns ranged in length from 40 to 240 feet. The kiln lengths were as follows: 40 to 60 feet, 208 kilns; 60 to 90 feet, 149 kilns; 100 feet, 84 kilns; 110 feet, 140 kilns; 120 feet, 86 kilns; 125 feet, 163 kilns; 125 to 140 feet, 60 kilns; 150 feet or more, 26 kilns.

The gains were all in kilns 100 feet or more in length and these gains more than balanced numerically the smaller kilns which were shut down, giving a total of 559 kilns 100 feet or more in length in 1911 as against 473 kilns in 1910. The 125-foot kiln is apparently still the most common length for modern kilns. From the reports received, it is apparent that the total annual capacity of the country in 1911, allowing for reasonable loss of time for repairs, should have been about 112,500,000 barrels, and that the total production of 78,528,637 barrels represented about 70 per cent. of the total capacity. The capacity in 1911 increased 14,830,000 barrels, or far in excess of the actual increase in production. The apparent average output per kiln in 1911 was about 85,730 barrels, as compared with 84,867 barrels in 1910. This increase is explained by the greater average size of the kilns operated during 1911. According to the mill reports all but about 30 of the producing plants in the United States were shut down part of the time for causes other than repairs, for periods ranging from 2 to 10 months. Shutdowns for repairs ranged from 2 to 6 weeks. The following 9 new plants reported their first commercial output in 1911: Golden State Portland Cement Co., Oro Grande, Cal.; Piedmont Portland Cement Co., Portland, Ga.; Lehigh Portland Cement Co., Mason City, Iowa; Chanute Cement Co., Chanute, Kans.; Tidewater Portland Cement Co., Union Bridge, Md.; Michigan Portland Cement Co., Chelsea, Mich.; Knickerbocker Portland Cement Co., Hudson, N. Y.; Clinchfield Portland Cement Corporation, Kingsport, Tenn.; and Inland Portland Cement Co., Metaline Falls, Wash. In addition, one plant in the Lehigh district, which was idle in 1910, reported a production in 1911. Against these there were 6 plants idle in 1911 that produced cement in 1910, distributed as follows: One each in Arizona and Pennsylvania, 2 in Michigan, and 2 in New York.

A committee composed of Government engineers and representative consumers and manufacturers, and of the national engineering societies, has recently formulated a set of specifications for Portland cement to be used by all departments of the Government. These specifications are described in the advance chapter from Mineral Resources on cement production for 1911.

The importance of testing cement just before using it is generally recognized by large consumers, but it is entirely overlooked by the great majority of those who employ cement on a small scale, as in building sidewalks and small houses, cementing cellars, etc. These suggestions are therefore addressed only to consumers who have ever looked into the matter of having tests made. A few important reasons why tests are essential are as follows: On account of the nature of the manufacture of cement from raw materials which are rarely constant in composition, the resulting product can hardly be expected to be invariably uniform. Manufacturers generally take precautions to prevent the shipment of defective cement, but the tests made at the mill cannot always reveal imperfections in manufacture. The properties in cement are subject to alteration after leaving the mill. Cement that is found slightly inferior when tested at the mill may be sold where it is not likely to be tested. Cement that is tested by large purchasers at the mills and rejected by them may be sold to smaller consumers.

In order best to ascertain the quality of cement shipped the tests should be made after the cement arrives on the work, and they should be made with the greatest care and only by responsible and trained men in laboratories where the instruments have been properly standardized.

For the purpose of correcting any misapprehensions that may arise it should be stated that the United States Geological Survey maintains no testing laboratories and does not make any kind of tests of cement or of any other structural materials either free or for compensation. Such work should be intrusted to private commercial laboratories, such as are in operation in all the large cities of the United States.

In response to a demand for a way in which to render cement mortar and concrete water-tight, a series of tests were carried on at the Structural Materials Laboratories of the United States Geological Survey at St. Louis, Mo. This work has since been transferred to the Bureau of Standards and the unpublished data delivered to that bureau. These data, which have recently been made public, have received attention in this paper.

Tests of iron ore cements and of various Portland cements, both in sea water and in fresh water, which extended over 52 weeks, were made at the Atlantic City Structural Materials Laboratories, organized by the United States Geological Survey, but recently part of the Bureau of Standards. These tests are discussed in the chapter on cement.

Practical Chemistry for Engineering Students. By ARTHUR J. HALE, B.Sc., Lecturer and Demonstrator in Chemistry at the City and Guilds Technical College, Finsbury, with an Introductory Note by Professor R. MELDOLA, D.Sc., LL.D., F.R.S. London: 1912. Longmans, Green & Co. pp. xix + 192. Price, $1 net.

This book purports to offer a course in chemistry which is specially adapted to the needs of the prospective chemical engineer or of the student of engineering who would add some knowledge of chemistry to his equipment. The distinctive feature claimed for it is, "The teaching of the subject with a bias towards the use of materials familiar in constructive industry—a bias becoming more and more pronounced as the student progresses, and leading finally to actual specialization." The course, as laid down, is designed to cover one hundred and eight two-hour periods, of which forty-five to fifty are to be given to general inorganic chemistry, twenty-two to twenty-seven to simple qualitative analysis and volumetric analysis, and thirty-six to "quantitative analysis for engineers," which includes the examination of such materials as iron ores, coals, cements, alloys, and water. An appendix contains some twenty-five useful tables.

In his introductory note, Professor Meldola commends the principle upon which the above course is constructed, namely,

that of arousing and holding the interest of the student by the use of materials which are selected because of their "engineering" significance, as pedagogically sound, but he also warns against the danger of losing sight of "the educational, as distinguished from the technical value of the subject, of its discipline as mental equipment quite irrespective of immediate utility."

In the opinion of the reviewer, the course offered by Dr. Hale is very much of the sort to which these words of warning should apply. It is not, as it stands, a course which will lead to the mental development of the student, because he is not required to develop ability to observe independently (he is, in general, told what to look for or what will happen) or to reason from one observation to another. The attempt to cover the ground which should demand two college years in two hundred and sixteen hours must obviously lead to a superficial treatment of the subject, and it may fairly be questioned if, at the end, the engineering student has gained "practical chemistry." It is certain that this procedure will not train him as an engineer of any sort should be trained in an important field, and it is much to be regretted that the endorsement of this course by Professor Meldola seems to make it apply to "chemical engineers" who above all else should have a thorough grounding in all the main branches of chemistry, especially with respect to underlying principles and theories. In the absence of a statement by the author, it is always difficult to determine how far reliance is placed upon supplementary class-room instruction to round out the course, but in this instance the time allotted by the author (two hundred and sixteen hours) leaves little opportunity for class-room exercises.

The experiments in general inorganic chemistry are mostly quantitative, or semi-quantitative, in character. The directions for qualitative and quantitative analysis are brief, but generally well-chosen. The general statements of fact are often too brief and isolated to be of value taken by themselves.

The book is of interest as another conscientious attempt to meet a demand which is very insistent just now for a course which will afford adequate instruction for students of engineering with whom chemistry is a side issue, with the least possible expenditure of time. Thoughtful teachers, especially those concerned with earning or trade schools, will find many helpful suggestions whether they adopt the course as a whole or not.

H. P. TALBOT.

Snap Commercial Analysis. By FRED W. BABINGTON. Ottawa. Thorburn and Abbott, 1912, 68 pp. Price, $1.50.

From the preface it appears that the author is Analyst in the Custom Service at Ottawa, Canada. With the exception of urine, the topics considered are commercial articles of a varied nature. The title of the booklet leaves the reader somewhat in the dark as to its meaning, but illumination is afforded by the statement that the methods outlined or referred to "are notes from a rough notebook." This tells the tale but partly. The composition is bad, gross errors of spelling, punctuation and of formula abound, and typographical mistakes are frequent. Proof reading has evidently not been attempted. The author knows "of no general taste for the analine dyes" in essences, "but as a rule an ignition will reveal the characteristic napthol odour." The following directions will, no doubt, interest coal analysts. "Results depend largely on sampling, a small piece about the size of a hazel nut being broken off each lump and about 100 grams roughly ground. This is sieved through three sieves the first (coarse) rejected; second, medium, kept for moisture; the third used for volatile and fixed carbon and ash."

One's first thought is that the booklet was written in jest. However this may be, it is one for the serious analyst to let alone unless he seeks mild entertainment for a leisure moment or an additional argument for a censorship of chemical literature.

W. F. HILLEBRAND.

NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian, Chemists' Club, New York.

Analysis of Metallurgical and Engineering Materials. By HENRY WYSOR. L. 8vo., pp. 82. Price, $2.00. Chemical Publishing Co. Easton, Pa.

Analysis; Methods of Volumetric—Part II. By H. BECKERTS and O. LUENING. 8th Edition. L. 8vo., pp. 360. Price, $2.50. F. Vieweg & Sohn, Braunschweig. (German.)

Arsenic; The Estimation of Minute Amounts of—in Foods. By EDMUND CLARK AND A. G. WOODMAN. 8vo., pp. 7. U. S. Dept. of Agriculture, Bureau of Chemistry, Circular 99.

Carbon; Lexicon of the— Compounds. By M. M. RICHTER. Vol. 4. 3d edition. Lex 8vo., pp. 4751. Price, $50.00. L. Voss, Leipzig. (German.)

Celluloid and its Substitutes. By W. MAIN. 8vo., pp. 163. Price, $0.75. Gauthier-Villars, Paris. (French.)

Chlorids; The Electrolytic Decomposition of Alkali— by Means of Immovable Cathodes. Part I. By J. BILLITER. 8vo. Price $4.00. Wilhelm Knapp, Halle.

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Furnace; Chemical Arithmetic and Calculation of— Charges. By REGIS CHAUVENET. 8vo. Price, $4.00. J. B. Lippincott & Co., Philadelphia.

Glass and Glass Painting. By C. J. STAHL. 8vo. Price, $1.25. A. Hartleben, Vienna.

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Metallurgy; Text-book of Chemical Technology and—. By BERNHARD NEUMANN. 8vo., pp. 900. Price, $4.75. S. Hirzel, Leipzig. (German.)

Mine Explosions; The Prevention of—; Report and Recommendations. By VICTOR WATTEYNE, CARL MEISSNER AND ARTHUR DESBOROUGH. U. S. Bureau of Mines, Technical Paper 21.

Mine Gas; Ignition of— by Miniature Electric Lamps. By H. H. CLARK. pp. 5. U. S. Bureau of Mines, Technical Paper 23.

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Paper; The Treatment of— for Special Purposes. By LOUIS E. ANDES. Cr. 8vo., pp. 250. Price, $1.75. Scott, Greenwood & Son. (Translation.)

Perfumery; The Manufacture of Modern—. By H. MANN. L. 8vo., pp. 370. Price, $2.50. Verlag fuer Chemische Industrie. Ausburg. (German.)

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Producer Gas. By J. EMERSON DOWSON AND A. T. LARTER. 3d edition. 8vo., pp. 319. Price, $3.00. Longmans, Green & Co., New York.

Proteins; The Chemical Constitution of the—. By R. H. ADERS PLIMMER. 8vo. pp. 188. Price, $1.50. Longmans, Green & Co., New York.

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Steel; Its Metallurgy and Mechanical Treatment. By F. W. HARBORD AND J. W. HALL. 3d edition 8vo. pp 758 Price, $9.00 J. B. Lippincott Co., Philadelphia.

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RECENT INVENTIONS

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

ATTACHING RUBBER TO METALS.

English Patent No. 2,306 (1912), to E. R. Royston.

The claim is made that it has been found that alloys containing antimony are best adapted to the production of a "chemical" bond between rubber and metal on vulcanization. The most suitable alloy is said to consist of copper, $3^1/_4$ oz.; zinc, $1^3/_4$ oz.; and antimony, 3 oz. The proportion of antimony should, it is found, be decreased when the rubber contains a relatively large amount of antimony sulphide. When the metallic base to which the rubber is to be fastened cannot be conveniently made of this alloy, another metal may be plated with a coating of the alloy.

ALKALI SILICATES IN POWDER FORM.

English Patent No. 23,391 (1912), to Justice.

The patentee observes that an industrial need has long existed for a readily soluble alkali silicate (waterglass) in powder form, this being more convenient than the usual solutions, the use of which is precluded for such purposes as colors, etc.

The preparation of a water glass in powder form on a large scale has, however, been hitherto attended with serious difficulties. The water glass solution cannot be directly transformed into the dry state, because in the process of concentration a skin that is impenetrable by water forms on the surface at once; at best, only a more or less solid jelly is obtained.

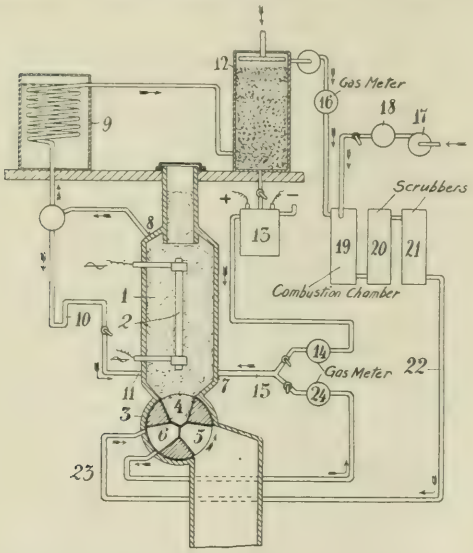
The present invention relates to a method of manufacturing fine-grained, readily soluble alkali silicates, by which the disadvantages specified are avoided and a product is obtained that is soluble even in cold water. The method consists essentially in bringing a hot, highly concentrated, thick solution of water glass (*e. g.*, solution of soda or potash water glass) under heavy pressure (for example, out of a pressure vessel, and through fine openings or spraying nozzles) into contact with cold air under relieved pressure. Under the heavy pressure the water glass assumes the form of spray, and after being suitably cooled, falls down as a dry dust.

The anhydride of sodium silicate is dissolved in water in an ordinary water glass autoclave in which a heavy pressure (about 6 to 8 atmospheres) is produced. The anhydride, being a fusion product, is a vitreous mass, which dissolves with difficulty; and therefore the dissolving process is preferably performed in a rotary apparatus under heavy pressure and at a high temperature, until the thick solution has a specific gravity of about 1.44. The resulting solution is thick while hot, and assumes, on cooling, the condition of a tough, set jelly. The hot solution is next forced out of the autoclave, under a heavy and constant pressure of about 8 atmospheres, through a spraying nozzle with orifices about 1½ mm. in diameter. The atomized solution is immediately transformed—under the influence of cold air—into a dry, solid condition. This operation is assisted by causing the dusty material to ascend through a shaft, for instance by means of a fan, and then allowing it to fall gradually to the ground as a perfectly dry powder.

PROCESS OF BINDING AND UTILIZING ATMOSPHERIC NITROGEN.

U. S. Patent No. 1,031,477, to Alf Sinding-Larsen, Assignor to Messrs. Storm, Bull & Co., of Christiania, Norway.

In the practice of this process to produce silicon nitrogen compounds of varying nitrogen content, a mixture of coke and quartz is heated to a white heat in a blast furnace. Somewhat above the bottom of this furnace, a mixture of nitrogen and chlorine is first introduced. Tetrachloride of silicon is formed which then reacts with the excess of quartz and coke to form silicon trichloride. At the high temperature present this trichloride will be acted upon by the nitrogen, so that silicon-nitrogen compounds are formed, then silicon tetrachloride is again formed, and so on. A part of the volatile silicon chlorine compounds is liable to escape, together with the carbon monoxide which is formed, and which has to be removed. In order to keep these back, the current of carbon monoxide is conducted through a suitable cooler, where the volatile compounds will be condensed and thereupon led back to the furnace.



HYDROGENATING FATTY MATERIALS.

U. S. Patent No. 1,026,156 to Carleton Ellis, Assignor to New Jersey Testing Laboratories, of Montclair, New Jersey.

This is a continuous process of treating unsaturated fats and the like by means of hydrogen or hydrogen adding substances for the purpose of saturating, to a greater or less extent, such unsaturated bodies, in order to raise their melting point or otherwise improve their quality.

The addition of hydrogen to unsaturated organic compounds as brought about by the catalytic agents has been the subject of many investigations, which embrace the work of Sabatier and Senderens, Mailhe, Henle, Willstatter and Mayer, Paal and Amberger, Paal and Gerum, Paal and Roth, Paal and Hartmann, Ipatiew and Philipow, Jakowlew, Rakitin and others.

In the practice of this process unsaturated fat is placed in the tank 1 and is allowed to flow slowly into the conduit 6 or 6*a*, respectively. Hydrogen gas or water gas is admitted through the pipe 18 as a counter-current, the hydrogen traveling in a direction contrary to the traveling liquid stream of oil. The conduit is inclined from the horizontal to secure any desired rate of travel of the oil stream. The latter flows past the stationary mass of catalytic material 7 while contacting with the counter-current of hydrogen. The heating jackets may be filled with paraffin wax or a fusible alloy maintained at the requisite temperature. The treated oil discharges at the lower end of the conduit through the pipe 20, and the spent or excess gas is removed by the pipe 22. When using a nickel catalyzer

Fig. 1.

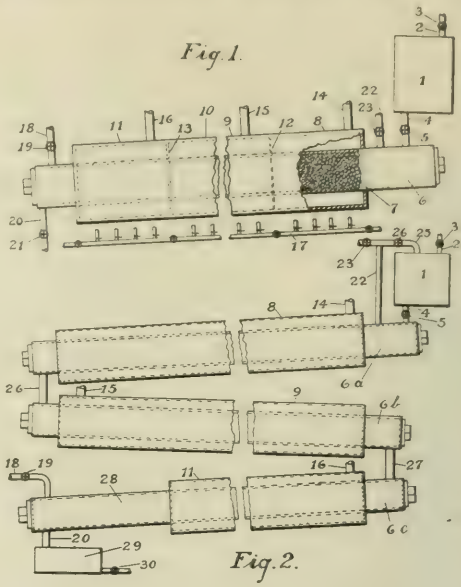


Fig. 2.

and differentially heating the conduit, the temperature in 6*a* may, for example, be 150° C.; in 6*b*, 165° C.; and in 6*c*, 180° C., when converting oleic acid or olein into stearic acid or stearin, respectively.

METHOD OF TREATING CARBON.

U. S. Patent No. 1,032,246, to William Acheson Smith, Assignor to International Acheson Graphite Company, of Niagara Falls, New York.

This is a process of treating carbon or carbonaceous material for the purpose of converting it in a progressive or substantially continuous manner into a homogeneous, uniform, commercial product. As between the several forms of carbon which may result from the application of heat to commercial carbonaceous materials, no mechanical separation is practicable, and it is essential in order that a given raw material may be converted throughout its mass into a commercial product of the desired density and electrical conductivity that the conditions as regards time and temperature of heating should be susceptible of accurate control and close adjustment, and that the heat should be so applied as to result in a practically uniform treatment of all particles traversing the furnace. According to this invention, the body of carbon or carbonaceous material to be treated is moved progressively through a heating zone located between terminals connected to a source of polyphase current, the arrangement of the terminals and the construction of the furnace being such as to secure a practically

Fig. 1.

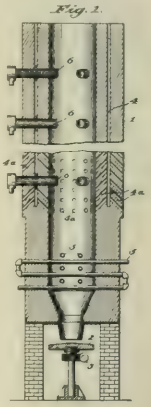
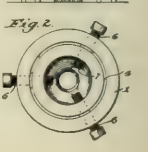


Fig. 2.

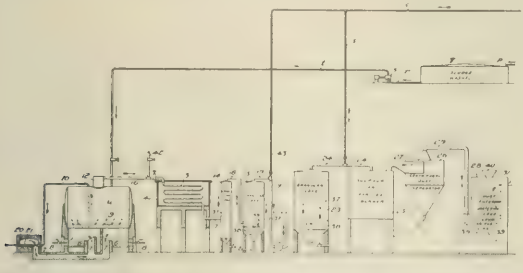


uniform heating of the entire cross section of the charge. One or more heating zones may be provided according to the results desired.

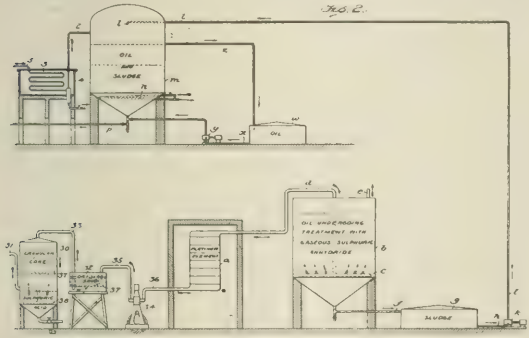
UTILIZING ACID SLUDGE FROM REFINING PETROLEUM.

U. S. Patent No. 1,031,413, to John C. Black and Marvin L. Chappell, of Richmond, California, Assignors to Standard Oil Company, of Richmond, California.

This is a process for utilizing the sulphur content of acid sludge for the production of sulphuric anhydride. The sludge is first heated in the presence of a solvent of hydrocarbons to effect a partial decomposition of the sludge. The solvent with the



hydrocarbons in solution is then withdrawn and the residual sludge subjected to a decomposing temperature (not above 425° F.). The aëriform products from both decompositions



are purified by contact with a solvent of hydrocarbons, the resulting aëriform products being passed over catalytic material for converting their sulphur dioxide content into sulphuric anhydride.

PRODUCTION OF LEAD COMPOUNDS.

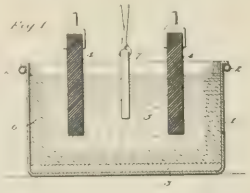
U. S. Patent No. 1,033,405, to Louis S. Hughes, of Chicago, Illinois, Assignor to Picher Lead Company, of Joplin Missouri.

A process of producing lead compounds such as lead hydrate, litharge, minium, lead carbonate, arsenate, nitrate, chromate and similar lead salts from lead sulphate. Lead sulphate is converted into lead hydroxide which in some cases is the ultimate product of the process and in other cases is an intermediate product thereafter converted into other compounds. In practice lead suphate and an alkaline base are placed in a grinding mill, a small quantity of water is added to the mixture, and the mass is thoroughly triturated. By triturating the wet mixture of lead sulphate and the alkaline base a thorough and rapid conversion of the lead sulphate is obtained. The trituration is effected in a double cone ball mill of well-known type, employing pebbles or metal balls. Crusts or coatings of lead hydrate are successively formed on and rubbed off of each kernel of the lead sulphate until finally the entire kernel is converted. After the conversion is completed the mixture of lead hydroxide and sulphate of the alkaline base is run out of the mill and the lead hydrate separated.

REFRACTORY ARTICLE AND METHOD OF MAKING IT.

U. S. Patent No. 1,030,999, to Samuel F. Hall, of Niagara Falls, New York, Assignor to Norton Company, of Worcester, Mass.

Attempts have been made to cast molten alumina or other refractory oxides or combinations of these in molds, but such efforts have not proved wholly successful. According to the patentee's process articles consisting of such refractory oxides are produced by heating the oxide, for example alumina, to a state of quiet fusion in an electric furnace, then dipping or immersing in the fused mass a mold or form, usually of carbon or graphite, withdrawing the mold together with the adhering or contained oxide, and separating or detaching the solidified oxide from the mold. By proceeding in this manner the patentee has found it practicable to produce a variety of articles, such as rods, tubes, vessels or the like, without flaws, cracks or objectionable irregularities, and, in the case of tubes or hollow articles, with any desired thickness of wall.

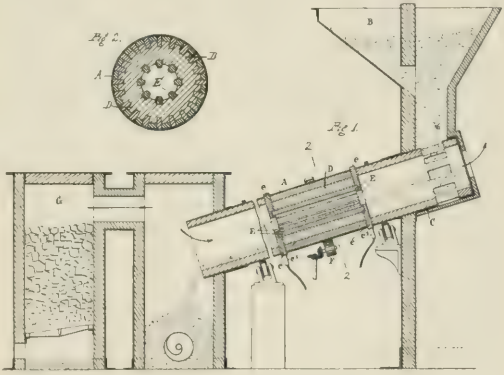


PROCESS OF MANUFACTURING ALUMINIUM NITRIDE.

U. S. Patent No. 1,030,929, to Ottokar Serpek, Assignor to Société Generale Des Nitrures, of Paris, France.

It is well known that if alumina be heated to a high temperature, for example in the neighborhood of 1800° C., in the presence of carbon and nitrogen it will combine with nitrogen to form aluminium nitride.

Heretofore it has been customary to pass an electric current through a mass of comminuted and intimately mixed carbon and alumina in an electric arc furnace through which nitrogenous gas is simultaneously blown. This is in a measure unsatisfactory, the heat beng too high in certain zones and too low in others. The patentee has discovered that this disadvan-



tage may be overcome if the mass is heated by being brought into contact with resistance elements through which alone the current passes. The resistance elements are preferably composed of a mixture of carbon and aluminium nitride and these, during the reaction, are set in motion so as to form stirrers which agitate the finely divided mixture of carbon and alumina and thus not only serve to evenly heat the mixture but to subject it more thoroughly to the action of the nitrogen which is blown through the reaction chamber.

MARKET REPORT.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF AUGUST.

ORGANIC CHEMICALS.

Acetanilid	Lb.	20½	@	23
Acetone (drums)	Lb.	17	@	18
Alcohol, grain (188 proof)	Gal.	2.55	@	2.57
Alcohol, wood (95 per cent.)	Gal.	50	@	52
Alcohol, denatured (180 proof)	Gal.	40	@	42
Amyl Acetate	Gal.	2.90	@	3.00
Acetic Acid (28 per cent.)	C.	2.00	@	2.15
Aniline Oil	Lb.	10¾	@	11½
Benzoic Acid	Lb.	23	@	27
Carbon Tetrachloride (drums)	Lb.	11	@	14
Carbon Bisulphide	Lb.	10½	@	11½
Chloroform	Lb.	20	@	30
Carbolic Acid (drums)	Lb.	15	@	16
Citric Acid (domestic), crystals	Lb.	38½	@	39
Camphor (refined in bulk)	Lb.	44	@	—
Dextrine (imported potato)	Lb.	6	@	7
Dextrine (corn)	C.	3.20	@	3.21
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	17¼	@	17½
Oxalic Acid	Lb.	7⅞	@	8⅜
Pyrogallic Acid (bulk)	Lb.	1.35	@	1.45
Salicylic Acid	Lb.	32	@	34
Starch (corn)	C.	2.43	@	2.54
Starch (potato)	Lb.	5¼	@	5¾
Tannic Acid (commercial)	Lb.	35	@	35½
Tartaric Acid crystals	Lb.	30½	@	31

INORGANIC CHEMICALS.

Acetate of Lime (gray)	C.	2.50	@	2.60
Acetate of Lead (brown, broken)	Lb.	7¾	@	8
Alum (lump)	C.	1.75	@	2.00
Ammonium Carbonate, domestic	Lb.	8¼	@	8½
Ammonium Chloride, gray	Lb.	6⅛	@	6¼
Aluminum Sulphate	C.	90	@	1.75
Aqua Ammonia (drums) 16°	Lb.	2¼	@	2½
Arsenic, white	Lb.	4⅞	@	5⅛
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Barium Chloride	C.	1.40	@	1.55
Barium Nitrate	Lb.	4¾	@	5
Borax, crystals (bags)	Lb.	3½	@	4
Boric Acid, crystals (powd.)	Lb.	7	@	7½
Bromine, bulk	Lb.	25	@	30
Bleaching Powder (35 per cent.)	C.	1.30	@	1.50
Barytes (prime white, foreign)	Ton	18.50	@	22.50
Blue Vitriol	Lb.	5½	@	5¾
Calcium Chloride	C.	65	@	90
Chalk (light precipitated)	Lb.	4½	@	6
China Clay (imported)	Ton	11.50	@	18.00
Feldspar	Ton	7.00	@	9.00
Fuller's Earth, powdered	C.	80	@	85
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1.15	@	1.55
Iodine (resublimed)	Lb.	3.05	@	3.10
Lead Nitrate	Lb.	8¼	@	8½
Lithium Carbonate	Lb.	65	@	70
Magnesite (raw)	Ton	7.50	@	8.50
Nitric Acid, 36°	Lb.	3⅞	@	4¼
Phosphorus	Lb.	35	@	90
Phosphoric Acid, sp. gr. 1.75	Lb.	22	@	26
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bromide	Lb.	31	@	34
Potassium Permanganate (bulk)	Lb.	9¼	@	9⅞
Potassium Cyanide (bulk) 98–99%	Lb.	19½	@	21
Potassium Iodide (bulk)	Lb.	2.60	@	2.65
Potassium Chlorate, crystals	Lb.	8¼	@	9½
Potassium Nitrate (crude)	Lb.	4¾	@	5
Potassium Bichromate, 50°	Lb.	6⅞	@	7
Quicksilver, Flask		42.50	@	44.00
Salt Cake (glass-makers')	C.	55	@	65
Silver Nitrate	Oz.	38½	@	40½
Soapstone in bags	Ton	10.00	@	12.00
Sodium Acetate	Lb.	4¼	@	5
Sodium Chlorate	Lb.	8¼	@	9½
Sodium Bicarbonate (English)	Lb.	2¾	@	3
Sodium Bichromate	Lb.	5⅛	@	5¼
Sodium Hydroxide, 60 per cent.	C.	1.70	@	1.75
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent., spot	C.	—	@	2.45
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	6⅞	@	7⅝
Sulphur, Roll	C.	1.85	@	2.15
Sulphur, Flowers (sublimed)	C.	2.20	@	2.60
Sulphuric Acid, 60° B.	C.	85	@	1.00
Talc (American)	Ton	15.00	@	20.00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	13¼	@	13½
Tin Oxide	Lb.	45	@	47
Zinc Chloride (granulated)	Lb.	4¼	@	4½
Zinc Sulphate	Lb.	2¼	@	2½

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	40	@	44
Black Mineral Oil, 29 gravity	Gal.	12	@	12½
Castor Oil (No. 3)	Lb.	9½	@	10½
Ceresin (yellow)	Lb.	9	@	15
Corn Oil	C.	5.90	@	5.95
Cottonseed Oil (crude), f. o. b. mill	Gal.	40	@	41
Cylinder Oil (light, filtered)	Gal.	19½	@	20
Japan Wax	Lb.	10	@	11
Lard Oil (prime winter)	Gal.	86	@	90
Linseed Oil (double-boiled)	Gal.	68	@	—
Paraffine Oil (high viscosity)	Gal.	25½	@	26
Paraffine (crude 120 & 122 m. p.)	Lb.	3	@	3⅜
Rosin Oil (first run)	Gal.	37	@	39
Spindle Oil, No. 1	Gal.	16	@	16½
Sperm Oil (bleached winter), 38°	Gal.	72	@	74
Stearic Acid (double-pressed)	Lb.	9	@	10
Tallow (acidless)	Gal.	62	@	65
Tar Oil (distilled)	Gal.	30	@	31

METALS.

Aluminum (No. 1 ingots)	Lb.	22	@	23
Antimony (Hallet's)	Lb.	7⅝	@	7⅞
Bismuth (New York)	Lb.	2.10	@	2.15
Copper (electrolytic)	Lb.	17½	@	17.55
Copper (lake)	Lb.	17½	@	17.55
Lead, N. Y.	Lb.	4½	@	4.35
Nickel	Lb.	50	@	55
Platinum (refined)	Oz.	46.35	@	47.00
Silver	Oz.	63	@	—
Tin	Lb.	45¾	@	—
Zinc	Lb.	6.95	@	7.15

FERTILIZER MATERIALS.

Ammonium Sulphate	C.	3.20	@	3.30
Fish Scrap, domestic, dried	Unit	2.45	&	10
Blood, dried	Unit	2.72½	@	2.75
Tankage, high grade	Unit	2.55	&	10
Bone, 4½ and 50, ground, raw	Ton	27.00	@	—
Potassium, "muriate," basis 80%	Ton	38.55	@	—
Phosphate, acid, 16 per cent.	Ton	7.00	@	7.25
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.	Ton	3.70	@	3.80
Tennessee, 68–72 per cent.	Ton	4.25	@	4.50
Pyrites, furnace size, imported	Unit	0.13⅛	@	0.13 /4
Castor meal	Unit	nominal		
Mowrah meal	Ton	8.50	@	9.00

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume IV OCTOBER, 1912 No. 10

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Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Penna., under the Act of March 3, 1879.

ESCHENBACH PRINTING COMPANY, EASTON, PENNA.

TABLE OF CONTENTS

INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY:

The Inaugural Meeting at Washington ... 707
The New York Meeting ... 711
The International Lectures ... 712
The Sectional Addresses ... 712
The Sectional Meetings ... 713
The Social Features of the Congress ... 713
The Closing Session ... 715
Factory Visits and Excursions ... 715
The Societies at the Congress ... 716

ORIGINAL PAPERS:

The Control of Dust in Portland Cement Manufacture by the Cottrell Precipitation Processes. By Walter A. Schmidt ... 719
Contact Sulphuric Acid from Brimstone. By G. W. Patterson and L. B. Cheney ... 723
Smelter Smoke Conservation. By George C. Westby. 725
Notes on a Study of the Temperature Gradients of Setting Portland Cement. By Allerton S. Cushman. 728
Cobalt Driers. By V. P. Krauss ... 731
The Development of Hydrosulphites in Their Relation to Modern Dyestuffs. By Philip S. Clarkson ... 733
The Effect of "Lime-Sulphur" Spray Manufacture on the Eyesight. By James R. Withrow ... 735
Phenol-Formaldehyde Condensation Products. By L. H. Backeland ... 737

LABORATORY AND PLANT:

Apparatus for the Examination and Study of the Behavior of Valve and Cylinder Oils and other Petroleum Lubricating Oils in Saturated and Superheated Steam, Carbon Dioxide, Air and Other Gases. By P. H. Conradson ... 744
A New Calorimeter Bomb with Special Advantages as to Material of Construction and Method of Operation. By S. W. Parr ... 746
Some Tests on a New Calorimeter Bomb. By Richard H. Jesse, Jr. ... 748

ADDRESSES:

The Latest Achievements and Problems of the Chemical Industry. By Carl Duisberg ... 749
Synthetic Ammonia. By H. A. Bernthsen ... 760
Progress in Industrial Chemistry. By Rudolph Messel. 767
Oxidation of Atmospheric Nitrogen and Development of Resulting Industries in Norway. By Samuel Eyde ... 771

CURRENT INDUSTRIAL NEWS:

A New Wood Preservative ... 774
Air Compressor Lubrication ... 774
The Oxygraph ... 775
The Manufacture of Lithopone ... 775
The Pollution of Streams by Spent Gas Liquor ... 776
The Melting Points of Fire Bricks ... 776
"Persil" as a Bleaching Agent ... 776
The Disinfection of Potable Waters by Chloride of Lime 777
Ammonia Evaporation and Transformation in Soils ... 777
The Location of Underground Pipes ... 777
The Casting of Magnesium Alloys ... 777

NOTES AND CORRESPONDENCE:

Obituary—Frederick J. Mayer ... 777
Third International Rubber Conference ... 778
Municipal Water Conservation Exhibit of the City of Philadelphia ... 778

NEW PUBLICATIONS ... 779

MARKET REPORT ... 782

INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY

The quest of knowledge has always developed friendships among men of different countries, and the mutual interest which exists among scientists has given rise to stronger bonds of coöperation than those produced by even the languages or political policies. In the last thirty years a movement, the direct result of the progress which the nineteenth century made in science, unparalleled in the history of the world, has eventuated in the organization of various International Congresses. This movement, really an endeavor to ascertain the most practical and efficient methods of scientific procedure, has fostered a uniform mental attitude which seems to have developed rapidly throughout the civilized world, and an intellectual union has been the consequence. The natural development of these organizations constitutes in itself a guarantee of solidity and efficacy.

WILLIAM H. NICHOLS, PRESIDENT.

There is to-day no German chemistry, no Russian chemistry, no Japanese chemistry, no American chemistry; there is one Universal chemistry, and in this respect our science differs from sciences in which the spirit is strictly national, as botany, seismology, etc. The psychology of the Orient and Levant may differ materially from that of the Occident, owing to the intellectual and moral differences in the peoples; but the chemistry of India and that of the United States are identical, because they are based upon uniform natural laws.

To the chemist belongs the honor of having first effected this great International movement—the convention of scientific men of varied nationalities. The initial international congress of chemistry was held at Carlsruhe in 1860; the meeting was attended by 140 chemists from all parts of Europe and lasted 3 days. At the Eighth International Congress of Applied Chemistry, 2500 chemists were present and the proceedings were of ten days' duration. The purpose of the Carlsruhe congress was the establishment of an international nomenclature. Although this congress was a success, yet more than a quarter century elapsed before the realization of the necessity of a similar convention was expressed. From 1889 on, the periods passing between the congresses of chemistry were of much shorter duration, thus, 1893, 1894, 1896, 1898, 1900, 1903, 1906, 1909, and 1912.

The first International Congress of Applied Chemistry was held at Brussels in 1894, and was the outcome of a suggestion of Doctor H. W. Wiley. This Congress was divided into four sections, *viz.*, sugar chemistry, agricultural chemistry, food and public hygiene, and biological chemistry. The Second International Congress of Applied Chemistry convened in Paris in 1896. Committees had been organized in various countries, and through the French Foreign Office all the principal governments were invited to send delegates; nearly 2,000 members were present, and the necessity of a close alliance between pure and applied science was shown. The Third International Congress of Applied Chemistry, held in Vienna in 1898, was divided into twelve sections; one of the principal questions before this Congress was the adoption of uniform methods of analysis for commercial products and raw materials. The Fourth Congress was held in Paris in 1900 at the time of the Grand Exposition; the work was divided into ten sections. At the Fifth Congress, in Berlin, 1903, of which there were 2,533 members representing 38 countries, about 500 papers were presented for discussion. Several German societies held their meetings in conjunction with this Congress, which was the most important and successful of all held up to that time. The Sixth International Congress of Applied Chemistry (Rome, 1906) was divided into eleven sections; the members numbered 2,375 and 658 papers were presented. The Seventh Congress (London, 1909), of which there were 4,100 members, was a worthy successor to the six preceding; 985 papers were presented in eleven sections and six subsections, and several innovations were arranged and carried out. A characteristic feature of the London Congress was the extension of the idea of the establishment of International commissions to recommend uniform standards of materials and methods of determining them.

The Eighth International Congress of Applied Chemistry, the most brilliant assemblage of men eminent in pure and applied chemistry ever brought together on this continent and a worthy successor of the preceding Congresses, officially closed its sessions on September 13, 1912, after ten days of scientific and social enjoyment—days which were replete with opportunities for affording direct interchange of views and during which Americans had the great

satisfaction of playing the part of host to those chemists who gathered from all parts of the civilized world.

This Congress, of which there were 4500 members, 2500 of whom attended the New York sectional sessions, had been an enormous undertaking and the immense amount of work which its preparation entailed devolved largely upon the President, Secretary and Executive Committee. It is to the President, Dr. W. H. Nichols, and to the Secretary, Dr. B. C. Hesse, however, that the greatest amount of credit is due for the splendid organization, elaborate arrangements and successful administration of the plans.

The Eighth Congress had been repeatedly brought to the attention of the chemical world during the past three years, and the plans of the organizers, both tentative and final, had been distributed throughout the world in a most thorough manner. The various Committees in charge of the many arrangements necessary did their work systematically, and earnest coöperation early marked the development of the many fixed rules and novel ideas introduced. It was only to be expected, therefore, that the Congress would have a number of features. One of the most important and valuable of these was that the bulk of the accepted papers was printed in advance in twenty-four carefully prepared, well-printed volumes, each devoted to a section. In this manner the greater amount of the papers presented were available for perusal and criticism prior to the sectional session openings, and

EDWARD W. MORLEY, HONORARY PRESIDENT

this arrangement not only encouraged attendance but also provided for more thorough discussion.

It has been said that the consciousness of a duty performed gives music at midnight, and it is agreed by all that the men and women who have worked and coöperated to make this Congress a success are entitled to unbounded credit and all the peace of mind which goes with a work well done. The success of the Eighth International Congress is a crowning event in the history of Applied Chemistry in America.

THE INAUGURAL MEETING AT WASHINGTON.

The official opening of the Eighth International

BERNHARD C. HESSE, SECRETARY.

Congress of Applied Chemistry took place at Memorial Continental Hall, Washington, D. C., on September 4, 1912, at 11.00 A.M. The Patron, President W. H. Taft, was unable to open the Congress personally on account of a sprained ankle, although he had made the trip from his summer home in Beverly, Mass., for the purpose; his regrets were presented by the President of the Congress, Dr. William H. Nichols. Dr. Nichols introduced the Honorary President, Dr. E. W. Morley, who made the following address:

"The Eighth International Congress of Applied Chemistry, assembled according to the invitation of the President of the United States of America, and by the authority of the Congress of the United States, desires to express its gratitude for this invitation, and further, its especial gratitude for, and high appreciation of, the honor done us, Mr. President, by your consent to open the deliberations of this Congress.

"It is my privilege, fellow members of the Congress, to express to you the cordial welcome with which the chemists of the United States receive you to their country. This cordial welcome we gladly offer to visiting chemists from every country of the whole world. Moreover, both the representatives in this country of applied chemistry, and also the lovers and followers of pure chemistry, take a special pleasure in welcoming chemists from the four nations whose languages are the official languages of this Congress. It was among these nations that, something like a

century ago, chemistry as we now understand it had its origin. Lavoisier established an anti-phlogistic chemistry, Dalton founded the atomic theory, Liebig furnished organic chemistry with methods, and Avogadro helped us to an insight into molecular weights. During the century since these magnificent beginnings, the progress of chemistry in these four nations has been well worthy of the beginnings.

"At the time of these brilliant beginnings the United States of America were but just become an independent nation. The work of the hour on this continent was to organize the mechanism of civilization in the wilderness which then covered much of our area. Pure chemistry had to wait while roads and bridges were built and the forest was cleared. Our studies and energies had to be expended upon the difficult problems of conducting a popular government—problems which we are optimistic enough to regard as not incapable of solution. The organization of universities by private initiative and expense, and the organization of elementary schools at public expense over almost half a continent, diverted able men from research in pure science. The necessities of mine and furnace and factory led men who might have stood high as investigators, to use their energy and insight in applying chemistry to industry, and adding to the wealth of the country and the comforts of life.

"Accordingly, the chemists of this country are delighted to welcome chemists from the nations who have been our masters and teachers in pure chemistry. The debt which we owe to the chemists of these nations is incapable of repayment. But if any courtesies which we can show you, any provision for the pleasure of your visit which we can make, any solicitude for the success of your deliberations which we can feel, should suggest that such repayment would be to us a privilege and a pleasure, and a great delight, we should but feebly express the warmth of the welcome with which we receive you to the sessions of the Eighth International Congress of Applied Chemistry."

President Nichols then made his formal address of welcome, which follows in full:

"On behalf of the great army of American chemists, more than six thousand in number, and representing all branches of the profession, and in the name of the great industrial organizations depending on their services, and also of the Universities, Colleges and Technical Schools, where many are devoting their lives to instruction, it is my privilege also to extend a hearty welcome to our guests from all the corners of the earth.

"We are gathered together to compare notes and to add to what has been done before, thus contributing to the great structure of the future something of perhaps vital importance to its growth and symmetry. We realize that this is an age of coöperation rather than of destructive competition, and we therefore unite our efforts that the resultant may be worthy of us. We are here to give, that we may receive, and thus pass on to the world something more than our isolated efforts could make possible. The alchemist of the middle ages worked alone, seeking the philosopher's stone, or perhaps the elixir of life, vainly hoping to transmute baser things into gold, or indefinitely prolong the joys of youth. We work together, and much has come to pass in the transmutation not of the elements, it is true, but of useless into useful things, and much has been accomplished in the betterment of the whole span of life. It is true we cannot see the goal and cannot even imagine what it will be when discovered in the distant future, but we are trying to do our share of the onward work, so that those who succeed us will be better prepared to take their part because of what we have done.

"Coöperation such as ours becomes not only a delight but a moral quality. To this symposium we, of the new world, cordially welcome those who from other lands and other experiences come to add their assistance and sympathy.

"To this word of welcome to our guests I am sure you would have me add one of appreciation of our Chairman, President Taft, who has torn himself away from a well earned and needed rest to come here to preside at this opening meeting of our Congress—a worthy successor of the kings and princes who have similarly honored those which preceded it. While his genial nature leads him to do this freely, we none the less appreciate that the chemists of the world, whether present with us or not, are under obligations to him which they can never repay. I am sure that I speak for you all when I tender to him our united thanks for the honor he has conferred upon us and on the science which we love.

"Since our last Congress, held in London in 1909, no past officials of the congresses have died. Sir Henry Roscoe, Hon. President of the Seventh Congress, has met with great affliction in the loss of his dear wife, but with that exception death has not entered into the homes of those who have presided over former congresses. We extend to him to-day our heartfelt sympathy, added to our regret that advancing age has prevented him from being present with us to-day. I am sure he is with us in the spirit.

"The President of the Fifth or Berlin Congress, Prof. Otto N. Witt, of Charlottenburg, has also been prevented from attending. I am sure that any one who has met him, or who has known of his great works, will join me in the expression of deepest regret that one of the most brilliant lights of the chemical world cannot be with us. Those of you who had the good fortune to hear his scholarly address at the Seventh Congress will, to some extent, appreciate what he could have added to this Congress had he been present.

"Prof. Emanuele Paterno, President of the Sixth or Roman Congress, finds himself at the last moment unable to attend. Up to a few days ago I felt sure of his presence, and was therefore all the more disappointed at his change of plans. We shall miss him greatly, although there are worthy representatives of his country here.

"We are very fortunate in having with us Professor Lindet, President of the Second Congress; Sir William Ramsay, President of the Seventh Congress; and Dr.

Friedrich Strohmer, of the Vienna Congress. These, with those I have named, are the only living members of the International Commission of Congresses of Applied Chemistry, and we are happy to welcome them and to know that we are to have the benefit of their great wisdom and experience during the conduct of the affairs of this Congress.

"I am pleased to report that a very large proportion of the original communications to this Congress has already been printed and bound, twenty-four volumes in all, and will be distributed to members on registration

A CONGRESS GROUP. Photo by *Harris & Ewing.*

SIR WILLIAM RAMSAY. DR. RUDOLPH MESSEL. PRES. W. H. NICHOLS.

at Columbia University on their return to New York. I think this is worthy of mention, as I believe it is a result which has never been accomplished before, and which could not have been accomplished now but for the magnificent and untiring work of our Secretary, and the coöperation with him of the officers and members of the Sectional Committees and the Committee on Papers and Publications. It is hoped that with these transactions in hand the discussions of the papers will be of great value. Thanks to the effective assistance of Mr. Edison and his staff, arrangements have been made to record these discussions on the phonograph in the official language employed, and this in itself will represent an added novelty in our Congress, and, at the same time, insure an accurate report.

"We are also fortunate in having some of the foremost chemists of Europe as lecturers on subjects of great importance; and, anticipating the public interest which these lectures will arouse, arrangements have been perfected to make them available for large numbers.

"The past fifty years have seen marvelous improvements in all branches of science. This is not the time or place to discuss details, but I feel justified in saying that the science of chemistry during the great evolutionary period has not been outstripped by any of the others. While its work has been more quiet, and has not been so obvious to the general public, it has been none the less of supreme importance. I believe it is gradually being realized that the world of the future will depend more upon the science of chemistry than upon any other, and may even have to look to it for its continued life. As its mines become more and more exhausted, and its lands more and more depleted of power to grow crops, it must turn to chemistry for instruction as to prevention of wastes and uses of power and materials, which, without its ministrations would be useless.

"With this thought in our minds we welcome with more than ordinary cordiality our foreign guests—some of them from the antipodes. We invite them to aid us in the solution of the great physical problems which confront us as a nation. We have had, and still possess, magnificent natural resources; we have perhaps done with them the best that we could, but we are becoming more and more alive to the fact that the problems are vast and complex. These natural resources must be exploited, but I conceive it to be of much more importance that they be intelligently conserved. The assistance of those who have of

necessity had these problems in conservation always before them will be doubly welcomed by us who have been so prodigal in the expenditure of our great wealth.

"The development of our country has been extremely rapid, but the thoughtful ones among us realize that the time is at hand when lavish expenditure must be succeeded by prudent conservation in order that we may not only pass down to posterity a record of wonderful evolution, but insure that we have not robbed our children's children of the materials necessary for their own progress.

"With these ideas we will proceed to our labors at New York with light hearts, believing that great good will come to our country and to the world as a result of those labors, not only in the immediate future, but more particularly in the more distant future which it is our bounden duty to carefully and religiously protect."

After President Nichols' address followed the official responses of the representatives of various countries: Prof. Dr. Rudolf Wegschneider spoke for Austria, Prof. L. Lindet for France, Prof. Dr. von Buchka for Germany, Sir William Ramsay for Great Britain, Dr. Jokichiro Lemori for Japan, Commanditore Giacomo Ciamician for Italy, Prof. Paul Walden for Russia, and Dr. Samuel Eyde for the other countries. Following these addresses, two resolutions were presented. Dr. H. W. Wiley presented a resolution of thanks to the D. A. R. for their permission to use the Continental Hall; Dr. D. T. Day moved that one copy of the official Congress badge be struck in pure gold, for presentation to the President, Dr. Nichols.

In the afternoon of September 4, there was a reception at the White House, and the delegates and their wives repaired thereto in large numbers, assembling in the East Room, where, after being introduced to the visitors, President Taft, seated in a wicker chair, said:

"Ladies and Gentlemen of the International Congress of Applied Chemistry:

"I have much pleasure in welcoming you, on behalf of the Government and people of the United States, to Washington. I sincerely hope that your stay in this Capital may be an agreeable one.

"Yours is one of those important International Congresses that mark the great progress which has been made in research and application of newly discovered principles in a most important science and art. If there be any science that goes to the heart of the matter, it is chemistry. Dealing with atoms and molecules and their association, and the manifestations of their action upon each other, chemistry seems at one time the most abstruse of sciences, and then when we see it applied in the great modern factories in the manufacture of those elements which are essential to the success of the industrial arts, we are made to know that the extent of the science from the theoretical to the practical is wider than that of any other.

"I observe that in your various divisions you discuss many different questions not peculiarly chemical. I note a consideration of the question of patents, what patents ought to include, and what kind of a patent system ought to be adopted by each Government. Patents have played a very great part in the development of the United States, and we have given to patentees a very valuable monopoly for the purpose of discovering by their industries, new methods of accomplishing useful results. Whether we have made this monopoly too great or not is now the subject of consideration by a Commission provided for by Congress. There is certainly great room for improvement in the machinery of our Patent Office, and it would be well if more value could inhere in the issuing of a patent as an evidence of real property. Now, however, until a patent has been fought through the courts, people do not seem to regard it as of a great deal of monopoly value.

"I may add that one of the great opportunities for reform, in my judgment, is in the shortening of patent litigation and the reducing of its expenditure. I know very little about chemistry, but I know a good deal about patent litigation. I know that the amount of money that has been unnecessarily wasted, and the inequality that has been produced between the rich litigant and the poor litigant, by reason of the unnecessary expense of that litigation, is one of the things that calls for remedy and immediate remedy. It is not essential that we should make a record of 10,000 printed pages at $50 a day for experts and $100 a day for patent lawyers. I have no objection to experts; I have no objection to patent lawyers: but I think we can have too much of both of them. What ought to happen is that the expert should be called into open court, should there be examined on the principal points of the case, and then dismissed, and not have that interminable system of records, which every Judge who has had any experience in respect to patent law must condemn, on the one hand, because of its uselessness, and on the other hand because of its expense. You observe that I am willing to make a diversion in the direction of which I know something. But it is not for me to discuss a subject that is only distantly related to the main purpose of your coming.

"I regret exceedingly that the weather is such as not to permit you to enjoy the beautiful grounds of the White House as fully as you could on a sunny day. I have come a long distance to meet you, in order to emphasize as much as I can the importance which the American Government and the American people attach to your deliberations and the subject matter of your consideration, and the anxiety and concern they have in promoting every International Congress which makes, as this does, for 'team-work' in the world's progress."

Upon the conclusion of this address, the party adjourned to the White House grounds, where the members were received by Mr. Taft, the introduction being made by Major Rhoads. This lawn party was a very pleasant affair and lasted from 5.00 to 6.30 P.M. The Marine Band, under the direction of Lieut. Santelmann, and assisted by Miss Agnes Hope Pillsbury at the piano, gave a most excellent musical programme. Refreshments were served in special tents, and the

terraces were crowded with friends and guests attending the Congress.

There were various private dinners in the evening, notably a "chemistry dinner" at the Raleigh by Dr. H. W. Wiley, but the principal social function was a reception by the Regents and Secretary of the Smithsonian Institution, held at the New National Museum. The latter, with its wealth of collections, including paintings, added interest to the function, which was in every respect a brilliant success. The Marine Band furnished a musical programme to which Mrs. Bertha Lincoln Heustis contributed a number of vocal selections. Dancing followed, in which the younger element participated.

work being greatly facilitated by having everything on one floor and in one room. Appropriate booths, properly numbered and named, were provided for registration, for general information in the four official languages, for United States branch post office, telegraph and telephone offices, railroad information bureaus, treasurer's office, factory inspection bureau, facilities for distributing printed proceedings, checkroom, express office, stenographers, etc. Official marshals were on hand to act as interpreters and assist the foreign members in registering and arranging their residence while at the Congress. The Columbia University Dormitory facilities were placed at the disposal of the visiting members by the Trustees, and

ENTRANCE TO COLUMBIA UNIVERSITY GROUNDS.

The following day many of the visitors went on a sight-seeing tour of Washington, and visits were paid to the various Government buildings and bureaus. In the evening of September 5, the Washington visitors left for New York to continue the formal work of the Congress.

THE NEW YORK MEETING.

The formal opening of the Congress in Washington was followed by the final registration and organization in New York City on September 6th. The work was centralized in the buildings at Columbia University on Morningside Heights, and at the College of the City of New York on Washington Heights. The Gymnasium in University Hall, the central building in the Columbia group, was converted into a series of offices for the administration of the Congress business, the the students dining room in University Hall was opened up to accommodate the visitors. Each section of the Congress was assigned a commodious meeting room in some of the buildings of the University group; the International public lectures, organ recitals and general meetings were held in the Great Hall at the College of the City of New York.

A daily Journal was published and distributed by the Congress and every detail of the administrative feature was carefully worked out for the comfort and convenience of the visiting members. The hospitality of the two great educational centers in New York—Columbia University and the College of the City of New York—contributed in a great measure to the success of this undertaking.

THE INTERNATIONAL LECTURES.

The important lectures which followed the sectional meetings on September 6, 9, 10, and 11, and which were open to the public, were delivered in the Great Hall of the College of the City of New York, by eminent members of the chemical profession from each nation represented in the four official languages, French, German, Italian, and English.

M. GABRIEL BERTRAND, *Professor of Biological Chemistry at the Sorbonne and the Pasteur Institute, Paris, France:* "THE PART PLAYED BY INFINITELY SMALL QUANTITIES OF CHEMICALS IN BIOLOGICAL CHEMISTRY." This lecture was delivered on September 6th in French, and embodied a scholarly summary of the results of years of study and experimental research conducted by the speaker.

GEHEIMER REGIERUNGSRAT PROF. DR. C. DUISBERG, *Managing Director of the Farbenfabriken of Elberfeld, Germany:* "THE LATEST ACHIEVEMENTS AND PROBLEMS OF THE CHEMICAL INDUSTRY." This lecture, delivered in German, was illustrated by lantern slides and extensive exhibits; it dealt most impressively and eloquently with the enormous strides which Germany has taken in the development of certain chemical industries, and was highly enjoyed by an audience of about 1500 persons. A full translation of Prof. Duisberg's lecture appears in this issue of THIS JOURNAL.

PROFESSOR WILLIAM HENRY PERKIN, *of Manchester, England:* "THE PERMANENT FIREPROOFING OF COTTON GOODS." Professor Perkin, who spoke, of course, in English, illustrated very forcibly the research chemist's services to the cause of humanity; his lecture which will be published in the next issue of THIS JOURNAL pertained to his discovery of a process for the permanent fireproofing of all kinds of cotton goods, and included a practical demonstration of its success.

PROFESSOR GIACOMO CIAMICIAN, *of Bologna, Italy:* "THE PHOTOCHEMISTRY OF THE FUTURE." This lecture, delivered in Italian, was of great practical importance on account of the suggestions it contained in regard to the better utilization of radiant energy.

All of the above general lectures, which were comprehensive and of great interest, were preceded by organ recitals and every facility had been provided by The Honorable Board of Trustees, President J. G. Finley, Professor Charles Baskerville, and Dr. W. L. Estabrooke of the College of the City of New York for the convenience of the lecturers and the reception of the audience. Each of the lectures was followed by a tea served on the College campus.

THE SECTIONAL ADDRESSES.

One of the interesting features of the Eighth Congress was the holding of joint sessions of various sections; at several of these joint meetings symposiums were held, while at three, important addresses were delivered by distinguished chemists.

DOCTOR SAMUEL EYDE, the eminent chemical engineer of Kristiania, Norway, addressed the joint meeting of the Sections on Inorganic Chemistry, Physical Chemistry, Electrochemistry, and Agricultural Chemistry, on September 7th in the Auditorium of the American Museum of Natural History. His subject was "THE OXIDATION OF ATMOSPHERIC NITROGEN AND DEVELOPMENT OF RESULTING INDUSTRIES IN NORWAY." This meeting was attended by the most prominent chemists at the Congress, as well as by many manufacturers and engineers, and will always be remembered by those present. An extended abstract of the address by Dr. Eyde appears in this issue.

HERR HOFRAT PROF. DR. HEINRICH AUGUST BERNTHSEN, *Managing Director of the Badische Anilin und Soda-Fabrik, Ludwigshafen,* delivered an address before the joint meeting of the Sections on Inorganic Chemistry, Physical Chemistry, Electrochemistry, and Agricultural Chemistry, at the Horace Mann Auditorium on September 11th, on

Courtesy of *American Druggist.*

HEINRICH AUGUST BERNTHSEN, PRES. BUNSEN GESELLSCHAFT.

"SYNTHETIC AMMONIA." This lecture was one of the most novel delivered before the Congress, and included a demonstration of the Haber process. The thanks of the meeting were voted to Professor Bernthsen for his brilliant lecture, the motion being made by Dr. Eyde and seconded by Professor Duisberg. Professor Bernthsen's lecture is reprinted in full in this number of THIS JOURNAL.

PROFESSOR WILLIAM HENRY PERKIN delivered a lecture on "THE POLYMERIZATION OF BUTADINE AND ISOPRENE," before the Sections on Organic Chemistry and India Rubber, on September 11. A large audience was present.

Prof. Perkin outlined the method of making synthetic rubber, which he recently described in a paper before the Society of Chemical Industry and then described a new method which he said looked very

promising. Since this new method has not yet been described we give its outline here:

Take ethyl alcohol, which may be easily oxidized to acetaldehyde. This is condensed by means of potassium carbonate to aldol and the aldol can be quantitatively converted into butylidine glycol. All the yields of these reactions are practically quantitative. The butylidine glycol is then converted into a chloride and passed over soda lime when practically the same product is produced as the isoprene from the isoamyl chloride and when treated with sodium gives even better rubber than isoprene.

Prof. Perkin exhibited samples of what he called the first synthetic rubber ever made (the product of Tilden).

THE SECTIONAL MEETINGS.

The scientific work of the Congress was organized in twenty-four sections. Each section was administered by a complete organization consisting of President, Vice-president, Secretary and Sectional Committee.

All papers offered to the Congress, after being passed upon by the proper Sectional officers, were submitted for final action to the Committee on Papers and Publications.

The greater portion of the Proceedings of the Eighth International Congress was printed in advance of the meeting, and issued to members on and after the morning of September 3rd. The Proceedings contained all accepted papers presented by June 30, 1912, and consisted of twenty-four volumes, including over 600 papers and over 5000 pages with illustrations.

The many additional papers read at the Sectional meetings but not submitted before June 30th, will be included with discussions of all papers in the Supplement to the Proceedings, to be issued before December 31, 1912.

Each volume of the Proceedings was devoted to a section. Thus authors were able to present their papers in abstract before the section and bring out a most complete and full discussion.

SECTIONAL DIVISIONS AND THEIR PRESIDENTS.

Analytical Chemistry: W. F. Hillebrand, Ph.D., Bureau of Standards, Washington, D. C.

Inorganic Chemistry: Charles L. Parsons, B.S., Technical Expert of Bureau of Mines, Washington, D. C.

Metallurgy and Mining: Joseph W. Richards, Ph.D., Lehigh University, South Bethlehem, Pa.

Explosives: Charles E. Munroe, Ph.D., George Washington University, Washington, D. C.

Silicate Industries: Allerton S. Cushman, Ph.D., The Institute of Industrial Research, Washington, D. C.

Organic Chemistry: Marston T. Bogert, LL.D., Columbia University, New York.

Coal Tar Colors and Dyestuffs: Herman A. Metz, 122 Hudson Street, New York.

Industry and Chemistry of Sugar: W. D. Horne, Ph.D., National Sugar Refining Co., Yonkers, New York.

India Rubber and Other Plastics: L. H. Baekeland, Sc.D., Yonkers, New York.

Fuels and Asphalt: David T. Day, Ph.D., United States Geological Survey, Washington, D. C.

Fats, Fatty Oils and Soaps: David Wesson, B.S., 24 Broad Street, New York.

Paints, Drying Oils and Varnishes: Maximilian Toch, 320 Fifth Avenue, New York.

Starch, Cellulose and Paper: Arthur D. Little, 93 Broad Street, Boston, Mass.

Fermentation: Francis Wyatt, Ph.D., 402 West 23rd Street, New York.

Agricultural Chemistry: Frank K. Cameron, Ph.D., Department of Agriculture, Washington.

Hygiene: W. P. Mason, M.D., LL.D., Rensselaer Polytechnic Institute, Troy, New York.

Pharmaceutical Chemistry: Joseph P. Remington, Ph.M., 1832 Pine Street, Philadelphia, Pa.

Bromatology: W. D. Bigelow, Ph.D., Department of Agriculture, Washington.

Physiological Chemistry and Pharmacology: John J. Abel, M.D., Johns Hopkins University, Baltimore.

Photochemistry: W. D. Bancroft, 7 East Avenue, Ithaca, New York.

Electrochemistry: William H. Walker, Ph.D., Massachusetts Institute of Technology, Boston.

Physical Chemistry: W. R. Whitney, Ph.D., General Electric Co., Schenectady, New York.

Law and Legislation Affecting Chemical Industry. The Honorable Edward D. White, Chief Justice of the Supreme Court of the United States, Washington.

Political Economy and Conservation of Natural Resources: J. A. Holmes, Bureau of Mines, Washington.

A prominent feature of the Congress was a number of joint sessions held for the purpose of a more general interchange of ideas and views on interrelated subjects. These joint sessions also gave excellent opportunities for the presentation of some of the most interesting and valuable lectures delivered during the Congress, notably those on "Oxidation of Atmospheric Nitrogen and Development of Resulting Industries in Norway," by Samuel Eyde; "Synthetic Ammonia," by Prof. Bernthsen; "Synthetic Rubber," by Prof. Perkin.

A list of the articles published in the proceedings and of especial interest to our readers can be found in the New Publications column of this issue. Many of the papers of industrial and engineering importance will appear in the current or subsequent issues of THIS JOURNAL.

THE SOCIAL FEATURES OF THE CONGRESS.[1]

One of the great advantages of an international congress is the opportunity offered for social intercourse; accordingly, the encouragement of frequent association among the members was carefully carried out by the Officers and Committees of the Eighth International Congress of Applied Chemistry,[2] and the entertainment of the visiting members was fully provided for. In fact, the social features of the Congress were almost equal in importance to the sectional meetings, for they gave every chance for *intimate* exchange of ideas and views.

[1] Exclusive of the entertainments and functions attending the Opening of the Congress in Washington, reported elsewhere.

[2] The Marshals, it may be mentioned here, did much to promote cordial acquaintances among the foreign guests and the home members.

The reception of the American Chemical Society to the members of the Congress at the Metropolitan Museum of Art, from 8.00 P.M. to 10.00 P.M. on the evening of Saturday, September 7, was a largely attended, highly enjoyed function. The Receiving Line, composed of twenty-eight Past Presidents and Officers of the Society and Officers of the Metropolitan Museum of Art, with their wives, and under the chairmanship of Dr. Arthur D. Little, formed at 8.30 P.M. in the Grand Foyer of the Museum, and from 9.00 to 10.00 P.M. a collation was served in the Trustees Room on the second floor. Members of the International Association for Testing Materials were also welcome with their guests. Through the courtesy of the Museum, a special illustrated program advising as to how best to see the collections and where they were located was distributed at the entrance. The Reception Committee, also under the chairmanship of Dr. Little, was made up of one hundred prominent American chemists; the Ladies' Reception Committee was

GREAT HALL OF THE COLLEGE OF THE CITY OF NEW YORK.

constituted of sixty-five ladies; and the Executive Committee on Arrangements, of which Dr. George F. Kunz was chairman and Dr. E. F. Roeber secretary, was made up of seventeen ladies and gentlemen.

Those members of the Congress holding entertainment coupons enjoyed a Boat Excursion up the Hudson River on Sunday, September 8; an Entertainment at the New York Hippodrome on September 11; a Baseball Game at the New York Polo Grounds on September 13. The Boat Excursion was attended by a large number of members and lady guests, the party leaving 41st Street and North River at 9.30 A.M. and returning late in the afternoon; the boat proceeded as far as Newburgh and during the trip refreshments were provided. The members who attended the production at the Hippodrome in the evening of September 11, which, like the baseball game on the 13th, attracted in particular many foreign visitors, were enjoyably entertained.

Among other social functions and entertainments, all of which were free to the members of the Congress, were the following: The inspection of the American Museum of Natural History on Saturday afternoon, September 7; the reception and entertainment by the Chemists' Club on the evening of September 10; the the Afternoon Tea and Exhibition of Photographs at the Camera Club after the joint meeting of the Section on Coal Tar Colors and Dyestuffs with the Sections on Paints, Drying Oils and Varnishes, and on Photochemistry; the Organ Recitals by Mr. Mark Andrews, of Montclair, N. J., on September 6 and 9, and the organ recitals by Professor Samuel A Baldwin on September 10 and 11, all in the Great Hall of the College of the City of New York; the Informal Teas at the College of the City of New York on September 6, 9, 10 and 11; and the Afternoon Tea on the lawn at Columbia University on September 12. There were in addition certain other functions taking place in connection with other organizations; on the evening of September 6, a number of receptions to foreign members in attendance and sectional smokers occurred. Throughout the Congress the Chemists' Club was the center of social activities; here many informal meetings and social gatherings took place. The reception and entertainment by the Officers and Trustees of this club to the members of the Congress, on September 10, was largely attended and highly successful. Dr. and Mrs. Morris Loeb gave a reception at the Chemists' Club for the Latin-speaking visitors, and, on the afternoon of September 11, the Italian delegation and their friends were entertained by the Italian Chamber of Commerce.

Among the private functions were the delightful lawn parties of Dr. and Mrs. Morris Loeb on September 8 and Mr. and Mrs. William James Evans on September 12. The charming garden-party of Mr. and Mrs. Evans was at Yattonhurst, Dobbs Ferry; the invited guests were conveyed to and from the reception in a special train. During the New York sessions a number of private dinners were given in honor of visiting chemists, the most notable of these being the ones of Dr. Hugo Schweitzer in honor of the Official Delegates of the English, German, French, Austrian and Italian Governments, at his residence on September 6; Professor Charles Baskerville, in honor of Sir William Ramsay, at the Century Association on September 6; and the several dinners of President W. H. Nichols, especially those on September 8 and 9.

The Grand Banquet of the Congress occurred on the evening of Thursday, September 12, at the Hotel Waldorf-Astoria. This dinner was attended by more than 1,000 members and ladies, and the Mayor of New York City, Hon. W. J. Gaynor, was the guest of honor

and principal speaker; addresses were also delivered by various American chemists, in which a welcome was bestowed upon the guests, and by English, French, German and Italian chemists, who referred appreciatively to the United States and Americans.

Mayor Gaynor, referred to by the toastmaster, President Nichols, as "the man who has the hardest job in all the world," regretted that he could not do justice to all the languages represented, hence his address was delivered in English. His remarks were partly on the public press, in the course of which he said that the newspapers had, during the Congressional week, given more space to stories of crime than to the proceedings of the world's great chemists. He also referred to socialism and requested the foreign representatives in his audience to take some of his statements on this subject over the seas with them for reflection.

Dr. John Huston Finley, President of the College of the City of New York, delivered an address on behalf of Governor Dix, of New York, in which he spoke in chemical metaphors. Dr. Finley's remarks were very entertaining and amused the audience immensely.

An unusual innovation for such an occasion was a speech by a lady. Mrs. L. H. Baekeland, Chairman of the Women's Committee of the Congress, spoke in a delightfully entertaining manner and was warmly applauded.

The list of speakers included: W. P. Wilkinson, representing Australia; Dr. Rudolph Wegscheider of Austria; B. Setlik of Bohemia; Paul Hagamans, Consul General of Belgium at Philadelphia; Dr. Anthony McGill of Canada; Prof. Belisario Diaz-Ossa of Chili; Mr. Yung Kwai of China; Dr. Don Guillermo Wills of Colombia; Dr. Einar Billman of Denmark; Prof. Leon Lindet of France; Prof. Dr. von Buchka of Germany; Rudolph Hofmann of Prussia; Prof. Gilbert T. Morgan of Ireland; Prof. G. Bruni of Italy; Prof. Adolfo P. Castanares of Mexico; Dr. Alfred Sinding-Larson of Norway; Mirza Ali Kuli Kahn of Persia; Dr. Paul Walden of Russia; Prof. Dr. Knut Wilhelm Palmaer of Sweden; Dr. F. P. Treadwell of Switzerland; Dr. James Moir of the Union of South Africa; and Sir William Ramsay of England.

The bearers of tickets for ladies accompanying members were welcome at all social functions, and the receptions, teas, organ recitals, general lectures, etc., were graced by the presence of many lady guests. A number of New York Ladies' Committees and Sub-Committees had been organized for the reception of the lady guests of the Congress, an enjoyable program had been prepared for the entertainment of these, and the Ladies' Committees did everything for the comfort and pleasure of the visiting ladies.

On Friday, Sept. 6, the General Meeting of all the Ladies' Committees (except the Reception Committee) took place at 10.00 A.M. at Columbia University; this was followed, in the morning, by an informal reception and welcome to the guests at Columbia University, and, in the afternoon, by a lecture on "Communal Work of Woman in America" in Rumford Hall, Chemists' Club. On Monday, Sept. 9, the lady guests enjoyed automobile trips in the morning, a luncheon at the "Claremont" at 1.00 P.M., and the informal tea at the College of the City of New York at 5.00 P.M. The following day, Sept. 10, the visiting ladies had, in the morning, the choice of one of the following two automobile trips, starting from the Chemists' Club: (1) Public Library, Tiffany's and the Metropolitan Tower; (2) Aquarium, Down-town Section, and the Stock Exchange. At noon the ladies and their gentlemen escorts visited Gimbel's Department Store; after this inspection a luncheon was served by Gimbel's in their Tea Room. Later in the afternoon a number of the ladies repaired to the College of the City of New York to attend the informal tea. On September 11, there were automobile trips in the morning and a concert in Rumford Hall, Chemists' Club, and an informal tea in the afternoon; the next morning an enjoyable boat excursion about New York Harbor, starting from 42nd St. and the North River.

THE CLOSING SESSION.

The Eighth International Congress of Applied Chemistry which had been in session in Washington and New York since September 4, officially closed with a business meeting at noon, September 13 in the Great Hall at City College. Dr. Nichols, the President, presided and a number of important business matters were considered.

A resolution to adopt Esperanto as the official language for the Congress was referred to the Ninth Congress for consideration and decision. The resolution to fix the periods for the meetings of the Congress five years apart instead of three was defeated and the meeting of the Ninth Congress was definitely fixed for 1915. The plan to standardize atomic weights for periods of five years instead of the present annual revision was changed to three years.

St. Petersburg was selected as the meeting place for the Ninth Congress and Professor Dr. Paul Walden, Professor of Chemistry, Polytechnical School of Riga, was elected President, and Professor Dr. Demetrius P. Konovaroff, Emeritus Professor of Chemistry in the University of St. Petersburg, and now Assistant Minister of the Department of Commerce and Industry in Russia, was elected Honorary President.

The gavel was formally passed by President Nichols to the newly elected President, Professor Walden, and the Eighth International Congress of Applied Chemistry, which was the most successful ever held, was officially closed.

FACTORY VISITS AND EXCURSIONS.

Great interest was shown by the visitors to the Congress in the facilities offered to inspect manufacturing plants. There was little time available for factory excursions during the meetings, but a number of very interesting trips were arranged for Saturday, September 14.

About one hundred and fifty members visited the Consolidated Gas Works at Astoria, L. I. This excursion was under the personal direction of Dr. Arthur

H. Elliott, the company's consulting chemical engineer; he was able to show the largest gas works in the world, producing both coal gas and water gas, in full operation. The Consolidated Gas Company furnished a special boat which transferred the visitors from the East 21st Street pier to Astoria and return.

The Corn Products Refining Company took a party of one hundred members under the guidance of their Chief Chemist, Dr. H. C. Humphreys, to their plant at Edgewater, N. J.

Dr. W. H. Nichols extended an invitation to about one hundred and fifty foreign guests to join a special boat trip to visit the works of the Nichols Copper Company at Laurel Hill, L. I. After inspecting the plant which has a daily output of 1,000,000 lbs. of refined copper, the party was entertained at lunch on board the boat during a short trip up Long Island Sound.

The Standard Oil Company conveyed a party of about two hundred visitors by special boat to their Queens County Works in Brooklyn. This excursion was under the direction of Mr. Gail Mersereau, formerly chemist for the Standard Oil Company, and Dr. Otto Kress, of Columbia University. The guests spent several hours in the plant and were keenly interested in the work.

One of the most interesting excursions in and about New York was the visit of a large party to the plant of the Bush Terminal Company in Brooklyn. This unique enterprise which constitutes probably the largest group of buildings in the world, planned for and devoted exclusively to various lines of manufacture, is located on the water front and is provided with every facility for the in and out transportation of goods.

On Monday, September 16, the excursions through the west left New York, *via* Pennsylvania Railroad. These excursions were organized by the Inland Transportation Committee under two heads to meet the convenience of the guests.

The Short Trip visits Philadelphia, Pittsburgh, Niagara Falls, Detroit, Chicago, Cleveland and Boston.

The Long Trip will extend to the Pacific Coast and will visit Philadelphia, Pittsburgh, Niagara Falls, Detroit, Chicago, Omaha, Denver, Glenwood Springs, Salt Lake City, Bakersfield, San Francisco, Los Angeles, Grand Canyon of the Colorado, Shreveport, New Orleans, Birmingham, Atlanta, Ducktown and various other points of interest in the south, returning to New York on October 22.

The Congress has organized along the entire route of these excursions, local committees for the entertainments of the guests, and much of the time will be devoted to the inspection of the principal industries of the localities visited. The two excursions are under the management of Dr. Geo. D. Rosengarten and Dr. David T. Day, both of whom will accompany the party throughout the trips.

THE SOCIETIES AT THE CONGRESS.

SOCIETY OF CHEMICAL INDUSTRY.

An informal reception was given at the Chemists' Club on Saturday, August 31, by the New York Section of the Society of Chemical Industry to visiting guests. This reception was very well attended. Refreshments and music helped to make the event enjoyable.

The Annual General Meeting of the Society was held on September 3, at 10 A.M., at the Chemists' Club. The address by the Retiring President, Dr. Rudolph Messel, is printed elsewhere in this issue.

RUDOLPH MESSEL, PRES. SOCIETY OF CHEMICAL INDUSTRY.

The following are interesting abstracts from the Report of the Council:

"The number of members of the Society is now 4273 as compared with 4300 at the last Annual Meeting. During the year 225 new members have been elected as compared with 245 last year; and the losses have been 253 as compared with 244 last year.

"The Journal in 1911 numbered 1478 pages of text besides supplement and advertisements, as against 1482 pages in 1910. On the recommendation of the Publication Committee, the list of British patent applications has been placed in the Supplement in such a way that it can be bound with the Journal if desired.

"The Council has appointed the President, Dr. Messel, F.R.S., to represent the Society on the Governing Body of the Imperial College of Science and Technology in the place of the late Dr. Divers, F.R.S. The Council will be glad to receive suggestions in connection with the establishment of an efficient system of education in Chemical Technology.

"Mr. Thos. Tyrer has been elected a representative of the Society on the Board of the National Physical Laboratory. A special Committee of the Laboratory has just commenced an investigation into the properties of glass for optical and other scientific purposes.

"The Society is taking part with other institutions in several inquiries of common interest; with the Textile Institute as to the dyeing of textiles with indigo,

with the Chemical Society into the possibility of so preparing abstracts as to avoid duplication, and with the Institute of Metals in considering the nomenclature of non-ferrous alloys. It has also taken part in a recent conference on the International Interchange of Students.

"The Royal Commissioners for the Exhibition of 1851, who have recently established a system of Industrial Bursaries, and are subsidizing young graduates in science who propose to take up industrial positions, have invited the Society to express its opinion thereon. Great diversity of opinion on the subject was expressed by the Sections, and the Council sent to the Commissioners a synopsis of the various views expressed. The Royal Commissioners have expressed their indebtedness to the Society for its assistance.

"The Society's medal, founded in 1896, and awarded once in every two years for conspicuous service rendered to Applied Chemistry by research, discovery, invention or improvements in processes, has this year been awarded to Sir William Crookes, O.M., F.R.S., for his epoch-making discoveries in physical chemistry and the rare metals.

"At the celebration of the 250th Anniversary of the foundation of the Royal Society, the Council was represented by the President of the Society who presented an address. A copy of this address appeared in the Journal for July 31.

"An International Exhibition will be held in San Francisco in 1915 to mark the opening of the Panama Canal, and the Board of Trade has expressed the opinion that Great Britain should take part in it. The Council of the Society is of the same opinion and trusts that the Exhibition will be supported by the Chemical Industry."

The President-elect of the Society is Marston Taylor Bogert, LL.D., Professor of Organic Chemistry in Columbia University.

The next annual meeting of the Society will be held in Liverpool, England.

The Annual Banquet of the Society of Chemical Industry, the most important social event of the annual meeting, took place on September 13th, at the Waldorf-Astoria Hotel. This banquet was attended by about two hundred and fifty persons, including many distinguished foreign guests.

The President, Rudolph Messel, Ph.D., F.R.S., occupied the chair, and the President-elect, Marston Taylor Bogert, acted as Toastmaster. The Toasts of the evening were:

"*The President of the United States,*"

"*The King of Great Britain and Ireland,*"

"*The Society of Chemical Industry,*" by Rudolph Messel, Ph.D., F.R.S.

"*New York,*" by Chas. F. Chandler, D.Sc., M.D., Ph.D., LL.D.

"*The Eighth International Congress of Applied Chemistry,*" by William H. Nichols, M.S., LL.D., D.Sc.

"*Our Guests,*" by J. Joyce Broderick, Esq., Acting British Consul.

"*The Ladies,*" by Mr. Lewis Sayre Burchard.

"*Science,*" by Sir William Ramsay, K.C.B., D.Sc., F.R.S.

VEREIN DEUTSCHER CHEMIKER.

After sight-seeing trips to Coney Island on Saturday, and in New York City on Sunday afternoon, the Verein met in Havemeyer Hall, Columbia University, on Monday, September 2, for a business meeting and lectures. The President, Geheimrat Prof. Dr. Carl Duisberg, occupied the Chair and made the opening speech, sketching the progress of the Verein from its foundation in Frankfort in 1887 by twelve German chemists, to the present growing membership of five

CARL DUISBERG, PRES. VEREIN DEUTSCHER CHEMIKER.

thousand. This meeting was a continuation of the 25th anniversary of the Verein held in Freiburg last Spring, and was largely attended, about three hundred and fifty people being present.

The Mayor of New York, represented by Mr. Speer, President of the Borough of Brooklyn, welcomed the Verein to New York.

Dr. Charles F. Chandler made the address of welcome (in German) for the American chemists. The Austrian chemists were represented by Prof. Dr. Rudolph Wegscheider, of Vienna. Official telegrams of welcome were sent to President Taft and the German Emperor.

Two lectures followed:

First: "*The Scientific and Technical Importance of Tar-phenols:*" Dr. F. Raschig, Ludwigshafen am Rhein.

Second: "*Thirty-two Years in the United States as Chemist and Manufacturer:*" Dr. F. W. Frerichs, of St. Louis.

The Verein took dinner at 1 P.M. at the Claremont Inn.

The ladies of the party spent the evening at the Knickerbocker Theatre, going to the Ritz-Carlton

Hotel for a collation after the performance.

The gentlemen attended a Kommers held by the Verein at Arion Hall. Dr. Hugo Schweitzer presided. The many addresses were well received. There were many salamanders and a "Bierspiel" full of typical German fun. The whole affair was one of considerable vivacity; the hall was crowded and the Kommers will remain in the memories of those present as a successful and enjoyable event.

AMERICAN CHEMICAL SOCIETY.

The Annual Meeting of the Council of the Society, presided over by President Arthur D. Little, took up the question of changing the dates of the annual meetings from July and December to the Spring and Fall months; this was discussed and is to be referred to a mail vote of the Society. Important changes

ARTHUR D. LITTLE, PRES. AMERICAN CHEMICAL SOCIETY.

in the Constitution were passed and recommended for adoption by the membership. A number of other business matters were disposed of and will be duly reported in the Proceedings of the Society.

The Regular Annual Meeting was held at the College of the City of New York, and took up only routine business. All of the scientific and social features which usually accompany the annual meeting were incorporated in the various functions of the International Congress.

The Society officially entertained the International Congress by a very successful reception at the Metropolitan Museum of Art.

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

The annual business meeting of the Institute was held in Rumford Hall, Chemists' Club, Thursday, September 5, with Dr. L. H. Baekeland presiding. The greater portion of the time was given over to a discussion of the report of the Committee on Ethics, Mr. G. W. Thompson, Chairman. After a few minor amendments, the report was adopted by the council and will now be submitted to the membership for approval, after which it will be published.

LEO. H. BAEKELAND, PRES. AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

The Institute banquet, which was very well attended by members and guests, was held in the dining-room of the Chemists' Club following the meeting. Dr. C. F. McKenna presided as toastmaster and responses were given by Dr. L. H. Baekeland, Mr. G. W. Thompson, Prof. Wm. P. Mason, Prof. C. F. Chandler, and Dr. Samuel Rideal of London.

Members of the Institute contributed a number of important papers at the sectional meetings and participated in all of the social events of the Congress.

CHEMISTS' CLUB.

The members of the Club constituted the reception wing of the Congress. They met the steamers, pro-

MORRIS LOEB, PRES. CHEMISTS' CLUB.

vided for the clearing and transportation of baggage, arranged hotel accommodations, and rendered invalua-

ble services in attending to the comforts of the visitors. The Club was a center of activity both in and out of season and its popularity as a meeting place and social center must have been a source of great pride to its officers and founders.

A number of brilliant receptions and entertainments were given at the Club, notably the reception to the visiting members of the Society of Chemical Industry on August 31, the luncheon to the members of the Society of Chemical Industry on September 3, the reception by Dr. and Mrs. Loeb to the Latin-speaking visitors to the Congress on September 2 and the Club reception to Congress visitors on September 10.

AMERICAN ELECTROCHEMICAL SOCIETY.

The twenty-second general meeting of the Society was held in joint session with the "Electrochemistry" section of the Eighth International Congress. In addition to the scheduled papers belonging jointly to the Society and the Congress, the following special papers were presented:

"On the Electrolytic Refining of Silver-Bismuth Alloys," by William N. Lacey.

"The Electrical Resistivity of Fire-bricks at High Temperatures," by A. Stansfield, D. L. McLeod and J. W. McMahon.

"Fixation of Nitrogen by Alumina and Carbon," by S. A. Tucker and Henry L. Read.

To avoid confliction with the special arrangements made by the different Committees of the Congress, no excursions or other special forms of entertainment were planned by this Society. The excursions of the

W. Lash Miller, Pres. American Electrochemical Society.

Congress, however, were open to those members who were also members of the Congress.

ORIGINAL PAPERS

CONTROL OF DUST IN PORTLAND CEMENT MANUFACTURE BY THE COTTRELL PRECIPITATION PROCESSES.[1]

By Walter A. Schmidt.

The control of the dust arising from the rotary kilns in the manufacture of Portland cement is continually becoming a more serious problem. This is partly the result of the enormous growth of the Portland cement industry which now demands factories of such magnitude that the large volumes of gases leaving the stacks carry enormous quantities of dust into the atmosphere, but is probably more directly attributable to the present trend of public opinion, which continually demands a more thorough control of fumes and smokes.

The question of the proper relationships which should exist between the factory and the surrounding inhabitants has become a very important social problem. At the present time a large amount of hardship is being caused by improper action on one side or the other, often substantiated by our courts on the ground of mere technicalities. This is a problem which should receive the closest and most thorough study by a competent body in an endeavor to establish such laws as will draw a line of equity between the different parties coming into contact through the development of our modern industries.

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

Should every smelter, refinery and like industry emit poisonous and noxious fumes from its stacks and all other factories permit smokes and dusts to escape in unrestricted quantities, life in any large industrial center would be unbearable. On the other hand, however, most industrial furnace processes cannot be conducted without the production of large volumes of gases which usually carry from the furnaces volatilized materials and solid particles, these solids being swept along by the heavy rush of the gases. As the factories grow in size and number the damage and "nuisance" caused by the fumes and dusts usually assume most aggravating magnitudes and, after a certain mark is reached, control of the annoying material in the stack gases becomes a necessity. At the outset we are, therefore, confronted with two conflicting factors, *first*, the one from within the factory, which in many instances makes it utterly impossible to prevent the formation of dusts, fumes and smokes in the manufacturing processes; and, *second*, the one from without, which makes it equally impossible to permit these materials to escape into the air, due to the damage to the surrounding country. A further complexity arises from the fact that the surrounding country very often demands the maintenance of the factory for its own continued prosperity.

It is readily seen, that to permit a problem of such conflicting interests to take its course without thorough

study and guidance, is bound to work hardship upon one party or the other, and, of necessity, will result in such unjust proceedings as have at times closed some of our most important industrial establishments or permitted other factories to continue causing damage to the territory surrounding them. A vital question confronts the people to-day in this regard,

FIG. 1.

in the establishment of a rational relationship between the different parties, taking into consideration the various questions entering into the rapid changes of our present-day industrial development.

The problem of relationships between factory and farmer has become extremely critical in Southern California with the cement industry, where the dust arising from the two large factories, the Riverside Portland Cement Company at Riverside, California, and the California Portland Cement Company at Colton, California, settled upon the orange and lemon groves in the vicinity, causing some damage. It would be out of place in this paper to comment upon the actual damage done, as all of the court testimony presented has so far thrown little light upon actual results. Whether the dust really does cause any injury to the trees is a question of minor importance in this particular locality, as the dust makes the groves unsightly and the farmers are convinced that actual damage has been done.

The Riverside Portland Cement Company experimented with numerous methods in an endeavor to control the dust arising from their factory, with little encouraging results, and two years ago the writer undertook the work of applying the Cottrell electrical precipitation processes to this new problem.

The Cottrell processes were invented and developed by Dr. F. G. Cottrell, now of the United States Bureau of Mines, but until recently of the Chemistry Department of the University of California. These processes were first developed in connection with the problems arising in the manufacture of sulphuric acid by the contact process. After the successful control of these acid mists, the processes were applied to smelter fumes, aiming directly at the control of the sulphuric acid in these gases. The first plant has now been in steady operation for over five years, operating upon the parting flue in the refinery of the Selby Smelter on San Francisco Bay. The processes were later applied to the larger problem of general smelter fume control. No attempt will here be made to go into detail regarding the work with these processes in this field, as the early history of the processes was quite thoroughly discussed in an article published a year ago in THIS JOURNAL[1] and has since been extensively abstracted in other journals.[2] Further, Mr. Linn Bradley is presenting a paper to the Metallurgical Section of the Congress upon the recent work done in this field of application.

In undertaking the application of the Cottrell processes to the problem of collecting the dust in cement mills, a large number of new factors had to be dealt with, as all work done previously had been conducted upon cool moist gases either containing large quantities of water vapor, acid fumes or similar materials, all of which gave distinct electrical characteristics to the gases. The primary factors in cement work are dry non-conducting gases, non-conducting dust particles, intense temperatures, large volumes of gases and large quantities of solid material carried by the gases. It is a fair estimate to assume as an average figure that a rotary kiln 100 feet long and 7 feet in diameter, oil-fired as on the Pacific Coast, has a volume of stack gases of 50,000 cubic feet per minute; the gases above the combustion zone in the stack have a temperature of about 450° C. and carry dust aggregating between four and five tons per day of twenty-four hours.

FIG. 2.

[1] "The Electrical Precipitation of Suspended Particles," THIS JOURNAL, Aug., 1911.

[2] *Mining and Scientific Press*, Aug. 26, 1911; *Scientific American Supplement*, Sept. 30, 1911; *Engineering and Mining Journal*, Oct. 14, 1911; *Engineering News*, Oct. 26, 1911; *Metallurgical and Chemical Engineering*, March, 1912; *Cement and Engineering News*, April, 1912; Rauch and Staub, April, 1912.

The plan which was first suggested for handling these gases was to turn all gases from the entire factory into one general flue and conduct them to such a point as would bring the temperature within the region of our past experiences. It was soon found, however, in our first tests, that the dry gases presented entirely different electrical characteristics than were encountered in treating the gases from smelter stacks, and it was later found that the high temperature facilitated the uniformity of the electrical discharge. The plan adopted therefore was to treat the gases at as high a temperature as was permitted by the properties of the structural material used in the treating apparatus. By using ordinary steel, it is quite possible to work at the average temperature of the stack gases, namely 450° C., provided however that the abnormal temporary rises in the temperature in these gases are prevented. The question necessarily arose regarding the possibility of maintaining satisfactory factory operation if we attempted to regulate the stack temperature too closely; extensive tests were undertaken in pyrometric control of the same. Work done during the past year has shown that by installing recording pyrometers in the proper place in the stacks and placing the instruments so that the "burners" can keep close watch upon them, it is an easy matter to regulate the fires in such a way as to give practically a uniform temperature in the stacks.

It was the first plan at the Riverside Portland Cement Company to connect all ten stacks by a common flue which should conduct the gases into a general treating apparatus, but the factory engineers decided that it would be preferable to maintain individual control of the kilns. As the factory design was such as to prevent installing this form of apparatus upon the ground, it was decided to allow the entire stack structure to remain intact and treat the gases after they left the existing stacks. These stacks are eighty feet high

Fig. 3.

and at this level has been constructed a platform upon which the entire apparatus has been placed. In order to test out what effect the apparatus has upon the kiln conditions, we passed the gases through the treater and directly into the air alternately without having the "burners" know the direction of flow of the gases. Sensitive recording radiation pyrometers failed to indicate any effect, either in the temperature of the stack gases or of the burning zone in the kiln.

It might be well here to say a few words regarding

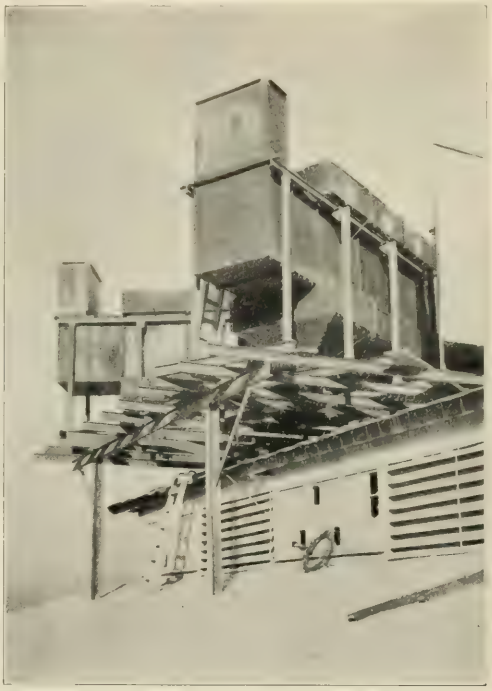


Fig. 4.

the underlying principle of the Cottrell electrical precipitation processes, for those who are not acquainted with them or who have not the time to read the references cited. The principle consists of bringing the dust-laden gases under the influence of a series of electrodes, some of which maintain a "silent" or "glow" discharge. By virtue of the discharge, the space between the electrodes becomes filled with gaseous ions and the dust particles passing through this space become charged by having these ions impinge upon them, imparting their ionic charges to the particles. The charged particles are then passed through an intense electric field which causes them to migrate in the direction of the field, which in the commercial apparatus is arranged transverse to the direction of the flow of the gases. The dust particles are by this action drawn out of the gases and deposited upon the electrodes, the gases being permitted to go their way unaffected and emerge from the treating apparatus freed from the solid particles which had been held in suspension.

The distinct advantage which this process has over mechanical processes arises from the fact that the

gases themselves play no part in the action in the treater, except as carriers of electricity. In all mechanical processes the entire volume of gas must be acted upon in such a way as to take advantage of the differences in specific gravity between the suspended particles and the gases themselves, or some similar

FIG. 5.

action. In electrical processes the gases are permitted to pass through the apparatus unaffected while the particles themselves are taken hold of individually by the electrical field and acted upon in such a manner as to draw them out of the current of advancing gases and precipitate them upon the collecting electrodes. In order to maintain a definite direction of migration of the dust particles, the electrodes must be given a unidirectional electrostatic charge which, in the commercial apparatus, is generated by rectifying a high tension alternating current. In the commercial apparatus the potential varies under different conditions from 20,000 to 40,000 volts.

The electrode system consists of two forms of electrodes: *first*, the discharge electrodes, which are made in various forms, depending upon conditions, but are always of a light construction and are so chosen as to maintain a heavy electrical discharge from them; *second*, the collecting electrodes upon which the solids are precipitated. These are usually of a heavy construction and the form and arrangement are so chosen that no discharge takes place from their surface. The two forms of electrodes are alternated across the apparatus with an electrode spacing of from two to six inches, this distance varying with the conditions to be met. A series of these rows of electrodes is placed in the treater so that the dust particles are brought under the successive action of this series of electrodes. The length of the treater is so chosen as to affect the desired cleaning of the gases. The cross section of the apparatus is made such as to bring a balance between the two forces acting upon the suspended particles, namely, the frictional force tending to carry the solid particles along with the gases and the electrical force tending to draw the suspended particles out of the advancing current of gases.

In the installation at the Riverside Portland Cement Company the treater has a cross section of 12 × 16 feet, and an over-all length of 20 feet. As stated above, the apparatus is placed upon a platform constructed at a height corresponding to the top of the original stacks, namely, 80 feet above ground. Upon this platform is placed a short stack extension which extends through the roof of the building structure and is supplied with a damper of special design. Upon either side of the stack is placed a complete electrical treater separated from the stack extension by a large louvre damper. By means of these three dampers, the gases can either be conducted through one or the other or both treating chambers or emitted directly into the atmosphere as occasion may warrant. Each stack is equipped with two treaters so as to have an auxiliary apparatus for each kiln. In case one treater should be shut down for repairs, cleaning or the like, the other treater will be able to take care of the gases with moderate efficiency. Under normal conditions the gases are passed through both treaters, insuring a thorough cleaning of the gases. The electrode spacing is here chosen at 6 inches and there are twenty rows of discharge electrodes in series. The dust is precipitated upon the collecting electrodes which are

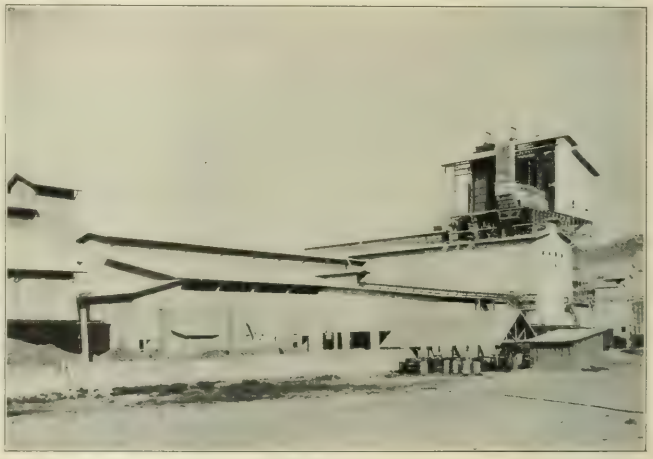


FIG. 6.

cleaned once every three or four hours by being given a mechanical rapping, this action being made automatic to the extent that the operator merely puts an electric motor into operation. The dust falls into hopper bottoms from which it is again conducted into the bins feeding the rotary kilns. Each treater is

supplied with a small outlet stack 20 feet high which is sufficient to compensate for the resistance offered to the gases by the treater. As stated above, sensitive pyrometers do not indicate any change of temperature in the kilns or stacks when the gases are permitted to escape directly into the atmosphere or are passed through the treater.

The operating costs of the apparatus are low. A complete treater of the size described consumes approximately $7^1/_2$ kilowatt hours. This includes electrical energy for all motors. A 5,000 barrel mill will, therefore, consume approximately 75 kilowatt hours in an entire installation. The manual labor required consists of one man per shift, of the character of men ordinarily employed to run electrical mill machinery. It is, however, usually advisable to have an extra man on duty. There is no deterioration in the apparatus under steady running and the machinery is subject to exactly the same wear as any other piece of electrical machinery.

In the series of photographs shown, Fig. 1 shows the factory as it appeared in 1910 with the experimental flue No. 1 and laboratory on the ground in front of the building. Fig. 2 gives a closer view and shows the initial experimental installation of two small precipitating units on the roof of the kiln room and just above the middle of the picture. The first full sized treater is at the right or opposite end of the row of stacks; Figs. 2 and 3 represent pictures taken 1 minute apart and show very plainly the effect of turning on the electrical current in the treater. In Fig. 3 the solid particles are all retained in the treater; the smoke from the other nine kilns is, of course, unaffected. Figs. 4 and 5 are views of experimental treaters built on the top of the stack. Fig. 6 is the first part of the permanent installation.

One important question which has grown out of the present work at the Riverside Portland Cement Company lies in the possible utilization of the collected material as a source of potash for fertilizer purposes. This factory does not use clay in its raw mix but a decomposing feldspar which has a considerable potash content. In the burning of the cement the potash is volatilized and condenses again in passing up the stack. The greater part is caught in the electrical treater along with the dust which gives a dust containing considerable potash value. Experiments have been conducted for some little time in the endeavor of utilizing this material either directly as a fertilizer "filler" or extracting the potash from the material with the aim of obtaining a concentrated potash salt. This work is not sufficiently far advanced to permit publishing definite figures.

Dr. F. G. Cottrell, inventor of the process, is presenting a paper to this Congress before the Section of Conservation and Political Economy upon what he has termed "An Experiment in Public Administration of Patent Rights." This deals with the recently organized "Research Corporation" to which Dr. Cottrell and his associates have given the Patent Rights to the processes for all of the United States except the six western states and the application of the processes to the Portland cement industry. These latter rights, along with the foreign holdings, are retained by the parent companies, the Western Precipitation Company and the International Precipitation Company, with offices at Los Angeles, California.

Los Angeles, California.

CONTACT SULPHURIC ACID FROM BRIMSTONE.[1]

By G. W. Patterson and L. B. Cheney.

The plant we purpose to describe was erected in 1907 at the U. S. Naval Proving Ground, Indian Head, Md., for the manufacture of acid used in making smokeless powder. It was designed by the New Jersey Zinc Co., which controls the Schroeder patents in this country.

With a rated capacity of six tons, it was operated successfully for three years, burning pyrites from New York and Virginia in O'Brien burners. During the last two years, Louisiana brimstone has been used entirely. The reason for changing raw materials was primarily to increase capacity without enlarging the plant, and it was hoped incidentally to reduce costs, notwithstanding the large increase in price per unit of sulphur. Our expectations have been fully realized in both respects.

The installation will be described under four heads: burner and gas cooling system, gas purifiers, conversion system, and absorbing system. The burner is housed in a detached frame building, 19 ft. × 32 ft., with sulphur store sheds adjacent. A frame building, 52 ft. × 60 ft., contains the conversion and absorbing systems. The gas cooling and purifying systems are in the open at the rear of the two buildings, in part protected by an open shed.

The burner is known as the Tromblee and Paull burner and has been most satisfactory. It consists of a horizontal cylindrical iron shell 8 feet long and 3 feet in diameter with conical ends, revolving on its axis once in two minutes. At one end is a hopper and worm feed with sliding dampers. The other end connects with a rectangular cast iron box of 37 cu. ft. capacity, provided with sliding damper and vertical cast iron uptake pipe. This pipe leads to a brick dust catcher such as is ordinarily used with pyrites burners. The dust catcher merely cools the gas, as no appreciable amount of sulphur is carried beyond the combustion box.

The burner is rated at 5500 lbs. per day, but there has been no difficulty in burning 6000 lbs. per day. Before feeding to the hopper, the sulphur needs no other preparation than breaking up large lumps with a shovel. When forced along by the worm, the sulphur melts just before it drops into the body of the burner, and a sufficient amount of melted sulphur is always present to form a complete liquid coating on the inside of the shell as it revolves. The combustion box and vertical uptake complete perfectly the combustion of any sulphur which is volatilized from the cylinder.

The special advantages of this burner are ease in controlling composition of gas, low cost of upkeep and

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

freedom from losses. Once in about two months it is necessary to clean out the dross which collects in the cylinder. To do this, or to prepare for a shut-down for repairs in any other part of the plant, the sulphur charge is allowed to burn out completely. Any residue in the cylinder is then easily removed by a hoe. Starting the burner after cleaning, or even when it is cold, is a simple operation and no losses occur.

At the exit from the dust catcher the gas has cooled to a temperature of about 230° C. At this point it enters the purifying system, consisting first of 250 linear feet of horizontal lead pipe arranged in tiers in a wooden rack. All gas passes through this total length of pipe. This pipe is cooled by a water spray, and here is deposited a small quantity of weak sulphuric acid formed in burning the sulphur. The acid deposited is, however, slight in comparison with the amount collected at the same point when pyrites was burned. The lead pipe connects with a large lead-lined box containing coke and here a further deposit of weak acid is obtained. Up to this point also is formed a slight deposit of carbonaceous matter from the asphaltic material which Louisiana brimstone always carries in small quantities.

From the coke box the gas passes to two wet scrubbers in tandem. Each scrubber outfit consists of a vertical lead cylinder with conical top, about 4 ft. high, a lead pot provided with lead cooling coils for water, and an air lift for circulating constantly a stream of sulphuric acid from the pot to the scrubber. The scrubber is divided horizontally by perforated diaphragms. The acid washes and dries the gas thoroughly and flows out through trapped pipes in a weakened condition to the pot. A pot holds 2500 lbs. of acid and is constantly strengthened to a gravity of 1.75 by the addition of strong acid. The excess acid formed at this point is collected in an egg and can be forced by air pressure to the weak acid supply used in the absorbing system. The air lift was designed by one of us (Patterson) to replace the ordinary bubbler formerly used. Only 5 lbs. air pressure is used, raising 80 lbs. of acid per minute, and the top of the lift is gas-tight, the air being piped to the gas system preventing any loss of SO_2 at this point.

From the scrubbers the gas passes to a second lead-lined coke box exactly like the first one and thence to a pair of dry filters in parallel. Each dry filter consists of three superimposed lead-lined iron trays luted together. Each tray contains a mat of dry asbestos fiber supporting a quantity of slag wool. A reserve set of these filters is kept ready for use as they require to be renewed about once in four weeks. The entire charge for two filters is 30 lbs. of asbestos and 400 lbs. of slag wool. The dry filters complete the purification process and the gas is then carried into the main building. Throughout the purification process the gas comes in contact with no other metal than lead, but beyond this point either cast iron or wrought iron is used entirely.

Within the house, the gas first passes through a positive pressure blower, by regulating the speed of which the composition of the entrance gas is controlled, and the movement of gas through the whole system is completed. Manometers on either side of this blower show a suction of 1.5" of mercury and a pressure of 0.75" of mercury. Just forward of the blower is the sampling pipe where the composition of entrance gas is tested by the usual iodine solution.

The next step in the process is the conversion system which includes a preheater and converter. The preheater is a series of vertical iron U pipes and headers housed in a furnace heated by soft coal to give to the gas an initial temperature of 380°C., this being required for proper catalytic action by the contact mass.

The converter is placed close to the preheater and is a vertical cast iron cylinder 6 ft. in diameter and $8^1/_2$ ft. high, composed of 5 horizontal sections. Each section contains a wire mesh tray for supporting the contact mass and a baffle to properly spread the gas. The contact mass is anhydrous magnesium sulphate carrying two-tenths of one per cent. metallic platinum in finely divided condition. A total quantity of 5900 lbs. of mass which is in coarse granules is spread on the trays to a depth of 14–16 inches, leaving a space of about 6 inches between mass sections. The gas enters the bottom of the converter and leaves at the top, pyrometer tubes being provided to read the gas temperature before entrance and in each section. From the converter the gas passes through 180 feet of iron pipe to the absorber. This pipe is air-cooled in order that the temperature of the gas may be sufficiently low for good absorption.

The absorbing system consists of a tower absorber, an acid-cooling pipe, a weak acid mixer and reservoir, a head tank for strong acid, an acid pump, and collecting tank. The tower is a vertical cast iron cylinder $15^1/_2$ ft. high resting on a cast iron base, the top being covered by a perforated plate from the center of which rises the exit pipe for waste gases. The tower is lined with acid tile and packed with quartz rock. The gas enters on one side near the bottom. A constant stream of acid is supplied by the pump to the top plate, percolates through the mass of quartz and passes out at the bottom of the tower to the cooling pipe. This is a horizontal water-cooled U pipe, one leg of which carries an overflow pipe connecting with the pump and the collector. The acid supplied to the top of the tower is kept at a temperature of 70° C. and has a strength of 99.5 per cent. H_2SO_4. The strength of the acid leaving the bottom of the tower is reduced by the constant addition of a small stream of 75 per cent. H_2SO_4 just before it enters the cooler.

The reservoir of this weak acid, the mixer and strong acid head tank are mounted on a platform in the center of the building at a sufficient elevation for the acid to flow by gravity. The reservoir is an open lead-lined box holding 1000 gallons. The mixer is a lead pot provided with lead coils for cooling water and a special mixing pipe designed by one of us (Cheney) in which water and strong acid are brought in contact. The mixing pipe consists of two heavy $^3/_4$" lead pipes set at an angle of 30° and held together by a heavy lead sheath burned onto a short length of $1^1/_2$" lead pipe. One of the $^3/_4$" pipes carries strong acid from

the head tank, and the other ordinary cold water from the mains. The $1^1/_2$" pipe serves to carry the hot mixture to the pot without spatter. This type has the advantage of minimum repair and mixes about 5000 lbs. of 75 per cent. acid per hour. The head tank has a capacity of 18,000 lbs. of strong acid.

The product of the plant passes through a scale tank and is delivered to the nitric acid plant where in winter weather it is mixed with 2 per cent. of nitric acid to prevent freezing. The entire product can be delivered as 99.5 per cent. H_2SO_4, but for use in making nitric acid a portion of it is reduced to 94 per cent. H_2SO_4.

This being a government plant the hours of labor for any one shift of men can not exceed eight. The plant is run continuously with three shifts and in addition to the men directly employed in the operation of the plant there is a superintendent who devotes about half of his time to it.

The successful operation of a contact plant, of course, depends largely upon the efficiency of the contact mass. This efficiency is easily influenced by arsenic in the raw materials. Should arseniuretted hydrogen be present in the gas entering the converter, arsenic is deposited on the platinum and is said to "poison" it. The result of "poisoning" is immediately noticeable in the temperature produced by. the catalytic action and in the quantity of SO_2 unconverted. Fortunately, this effect may in part be counteracted by raising the temperature of the gases entering the converter, and for this reason hardly any two plants burning pyrites will be found using the same initial temperature. In different plants we have noted temperatures of entrance gas varying from 420° C. to 480° C. The catalytic properties of "poisoned" mass may be improved by sprinkling it with aqua regia and expelling the arsenic by the heat of the converter, or they may be entirely restored by heating the mass in a furnace after sprinkling with aqua regia.

Another factor in conversion is the quantity of SO_2 contained in the gas entering the converter. With pyrites it is customary to use an entrance gas containing not over 5.5 per cent. SO_2 with mass in good condition. When "poisoning" has occurred, this percentage must be reduced to obtain good conversion.

In this plant, using Louisiana brimstone for eighteen months, we have had no indications of "poisoning" and have not opened the converter. The temperature of gas entering the converter is kept constantly at 380° C. and conversions are regularly 95–95.5 per cent. This low temperature means a decided saving in coal, and wear and tear on the preheater. During six months the average consumption of coal has been 21.8 lbs. per 100 lbs. of SO_3 made. We believe this to be a figure decidedly less than in any Schroeder plant burning pyrites. An entrance gas of 6.5–7 per cent. SO_2 is regularly used. During six months under the above conditions, the average make has been a little more than 6 tons of acid a day, and the average yield on sulphur fed to the burner 93.36 per cent. The plant can make a maximum quantity of 8 tons with a yield of 90 per cent. Comparison of cost sheets shows that by changing raw materials from pyrites to brimstone, we have reduced cost of manufacture nearly two dollars per ton of 98 per cent. acid; that this reduction is due in part to minimizing losses from shut-downs for repairs, in part to increased yields and in part to saving in coal and cost of upkeep.

U. S. Naval Proving Ground,
Indian Head, Md.

SMELTER SMOKE CONSERVATION.

By George C. Westby.

Received August 21, 1912.

The question of smelter smoke treatment is one of commercial metallurgy, and the application of a panacea a question of dollars and cents.

There have been many plans devised for quieting the complaints of injured agriculturists and others to whom smelter smoke seems all that is evil, but too often the proposed plan has been merely mitigatory, or has neglected provision for a material return on the investment in the plant. In other cases the process is rendered inapplicable on account of limited demand for the output whose production and sale is the vital commercial feature.

Of the methods projected for treating smelter smoke in an economic way, this article is limited to consideration of methods with which the writer has experimented.

The first of these was developed during 1902–1903 and consisted of a process for producing liquid SO_2 from the smoke, utilizing the heat of the smoke by means of economizers and air heaters. The SO_2 was to be liquefied by an ice or refrigerating machine, with the crystallohydrate of SO_2 as an intermediary product.

Aside from the mechanical difficulties incident to the arrangements for removing the flue dust, the crucial objection advanced against the process was the lack of a market for the liquid gas as produced at the rate of thousands of tons per day. The suggestion that it could be used as a refrigerant in place of ice in freight cars, and in the small ice boxes of private homes, seemed inadequate in face of the fact, that the market was both problematical and undeveloped while awaiting the expenditure of some millions of dollars in providing the necessary equipment.[1]

During the course of further work in connection with the smoke problem, the idea suggested itself that the sulphurous gases of the smoke might be bound with the bases of slag and thus reduced to a more controllable form. Experiment demonstrated that the idea might be practically applied, and also suggested the general method of smoke treatment which consists in the neutralization of acid fumes on slag, and ensuing precipitation of the toxic oxides in ponds or other limited areas on the earth, chiefly as harmless and insoluble compounds with iron and other bases of the slag. As developed, the process also involved the recovery of values carried by slag and flue dust.

[1] This phase of smoke eradication method was independently educed by Dr. Carpenter, of Denver.

The fact that chilled, finely divided slag very rapidly dissolves in hot dilute solutions of HCl or H_2SO_4, is generally known to metallurgists and chemists, and they are also acquainted with the fact that the silicic acid is retained in apparent solution. Experiment proved that hot solutions of SO_2 are also capable of effecting the dissolution of the slag in the same way; this discovery became the basis of our attack on the smoke difficulty.

In carrying out the process we have at command a hot acid smoke, laden with flue dust, vapors of sulphur and possibly arsenious or other volatilized compounds. We have also at hand granulated and chilled slag.

The acid smoke is an immediately available and intensely active chemical agent, but the granulated slag while susceptible to the vigorous attack of the sulphurous reagent, is preferably finely ground in order to accelerate its solution and incidentally reduce the size of apparatus required in its treatment. In conjunction with the smoke and slag, water or circulating ferruginous smoke liquor is necessarily used as a medium of chemical translation, in maintaining suspension of the slag pulp and in carrying the compounds formed. The slag and smoke are brought together by means of an apparatus which is introduced as a part of the flue systems. The province of the appliance is the retention of a vast surface of wetted slag in the direct path of the smoke current, in such a way that the smoke, slag dust, steam and water become as nearly as possible a hot homogeneous mist or spume.

Chemical action under such circumstances is essentially rapid, and ensures the absorption of the sulphurous gases without recourse to unwieldly apparatus or large chambers.

The result of the combination of the constituents of the mixture is the production of ferrous and ferric sulphite, ferrous sulphate, various thionates of iron and in a smaller degree sulphur salts of other bases.

The copper is mainly present in the matte particles contained in the slag, and when ground slag is used in the apparatus, remains for the most part undissolved. That portion of the copper taken in solution may be reprecipitated in the absorber by the action of polythionates developed in the smoke liquor through the interaction of the SO_2, sulphites and free sulphur of the smoke.

In many of our experiments copper was obtained principally in an oxidized form by blowing molten slag into slag wool. In these cases the copper was maintained in solution and after discharge from the absorber was precipitated in a wooden tank by heating the solution with steam to about 80° C.

The development of thionates, on which the precipitation of part of the copper depends, requires no attention under the usual circumstances attending the roasting of ore. Their formation is encouraged in the presence of the sublimed sulphur of the smoke, and by the sulphites and the excess SO_2 of the smoke liquors. During the course of their production, there may be a constant representation of all those compounds designated as polythionates, but the dominance of any particular form depends on the chemical and physical characteristics of the smoke, the liquor and the material treated. The thionates produced are ephemeral and finally break up into sulphates, sulphur dioxide and free sulphur as indicated in the following equation:

$$MS_nO_6 = MSO_4 + SO_2 + (n - 2)S.$$

To illustrate a possible set of conditions occurring in the absorber during treatment of the smoke, we may take the following successive reactions:

$$4FeSO_3 + 2SO_2 + O_2 = 2Fe_2(SO_3)_3.$$
$$Fe_2(SO_3)_3 = FeS_2O_6 + FeSO_3.$$
$$2FeS_2O_6 + S_2 = 2FeS_3O_6.$$
$$2FeS_3O_6 = FeS_2O_6 + FeS_4O_6.$$
$$2FeS_4O_6 = 2FeS_2O_6 + 2S_2.$$
$$6FeS_4O_6 + 4CuSO_4 = 2Cu_2S + 14SO_2 + 3S_2 + 6FeSO_4.$$

When sodium and potassium are present in the slag they are dissolved with the other constituents and later appear as sulphates in the discharged smoke liquors, and may be recovered if desired from the residues of the evaporated liquor. Zinc if present is similarly dissolved and may be separated from other residues by volatilization or any practicable means. Lead, silver and gold are retained undissolved with the precipitated copper. In some cases green vitriol would be an important and valuable by-product.

The liquor produced in the absorption chamber may be again used or it may be continuously discharged on waste land, over which it spreads in a thin sheet that will rapidly evaporate under the influence of wind and sun. In the latter case, oxidation and hydrolysis form an insoluble basic sulphate, by translation of the green vitriol in general accordance with the equation

$$4FeSO_4 + O_2 + 2H_2O = 4FeSO_4(OH),$$
or $$6FeSO_4 + 3O + 3H_2O = 2Fe_3(SO_4)_3(OH)_3.$$

At the same time deposition occurs of the silicic acid and of sulphur arising from the decomposition of thionates.

Generally the liquor issuing from the absorber contains only very limited quantities of free acid. If, however, any objectionable amount of acid is present, it may be neutralized by passing the liquor over slag or through calcareous or soluble ferruginous material. In some cases the percolation of the liquor into calcareous soil would not be objectionable, as the comparatively small quantity of acid would be effectually neutralized in the formation of insoluble calcium sulphate, and thus the liquor could not seriously affect the ground water.

The flue dust carried by the smoke is effectually caught by the somewhat glutinous slag particles, and remains with the residues of the reaction chamber.

In carrying out the experiments it was recognized that the development of a simple apparatus was of the first importance; accordingly much time was spent on different tentative designs, but the aim in each case was the form of apparatus which would require the minimum of attention, repairs and adjustment.

The arrangements tried were of two general forms:

a tower or vertical chamber and a horizontal rotary apparatus.

The vertical arrangement consisted generally of a wooden tower, provided with a large number of narrow staggered shelves. These pieces were set three or four inches apart, from one end of the tower to the other. A hopper was introduced at the top of the tower for the reception of the slag and water used in the treatment. The bottom of the tower was arranged to permit the formation of a hydraulic seal at the discharge. At each end of the tower pipes were inserted; one of these was connected directly with the flue of a furnace and the other with a fan.

In operation the wet slag was charged into the hopper and was discharged from the hopper by gravity to the shelves. From the top shelves the material spread over the cross section of the tower and by the action of the series of staggered shelves, fell in splashing cascades to the bottom of the tower, coming in contact throughout its course with the hot current of acid smoke drawn through the apparatus by means of the fan.

The liquor derived by the action of the smoke on the wet slag discharged through the hydraulic seal to a large wooden tank in which the copper was precipitated by means of steam. Wooden launders conveyed the residual liquor to a pond.

The horizontal rotary apparatus was cylindrical in form. Shelves or projections were set at intervals along the interior surface, so as to lift the mixture of slag and liquor and drop it in sheets through the smoke current in the apparatus. The shelves were set at different angles so that the material would be distributed along the different planes during rotation of the cylinder. The splashing on the sides and bottom of the apparatus caused by the falling material, aided in filling the whole of the cylinder with a constant spray of absorbent mixture.

The cylinder rotated about short pipes of comparatively large diameter; these were set at the smoke entry and exit ends of the cylinder and were connected respectively with the flue of the furnace and the intake of an induction fan. The treated smoke was discharged through the fan.

Means were provided for continuously feeding the absorbent material into the cylinder, and a pump with a syphon attachment was used in removing the exhausted liquor.

The first general test was made with a rotating cylinder. The cylinder was about 10 feet in length and 30 inches in diameter.

The results of one of the experiments with the apparatus are given below:

Time.	10.15.	10.45.	11.00.	11.15.
Temp. gas inlet ° F.	215°	220°	210°	242°
Temp. gas outlet ° F.	82°	84°	74°	74°
Temp. water inlet ° F.	64°	65°	65°	65°
Temp. liquor outlet ° F.	90°	100°	78°	86°
Cu. ft. gas per min. measured at intake.	34.2	32.4	33.0	44.4
Per cent. SO_2 inlet.	4.9%	4.7	5.4	4.7
Per cent. SO_2 outlet.	1.9	1.0	0.85	2.7
Absorption in 10 feet.	61.2%	78.8%	84.2%	42.5%

NOTE: 140 lbs of slag charged at beginning of test; none charged during interval between 10.45–11.15. The test gives results better than average, consequent on treatment of smaller volume of smoke per sec. than ordinary.

The test illustrates a set of experiments where the slag was not fed continuously, but was charged in one mass. The absorption in this case steadily increased for a short period after charging, then fell off rather rapidly. In the experiment given above the drop is accentuated by the increase of gas current.

In the experimental results given below the slag was practically continuously charged, although not in sufficient quantity to bring about complete absorption.

The tests were made with the tower apparatus of which the general principles have been described. Two towers were used connected at their tops. The total length of the apparatus was 77 feet. The cross section was 4 square feet.

	Temperature in Degrees Fahrenheit of				Cu. ft. gas	Per cent. absorption
Time.	ingoing gas.	outgoing gas.	ingoing water.	outgoing liquor.	per min.	SO_2 by volume.
10.00 A.M.	320	90	96	110	68.4	81.1
10.20	355	90	..	...	84.6	79.6
10.30	355	90	..	...	84.6	82.0
11.00	355	..	..	...	84.6	82.0
1.00 P.M.	350	..	96	109	112.2	74.8
1.20	340	..	..	...	85.8	79.1
1.35	345	..	..	...	85.2	81.1
1.4	350	..	..	...	91.8	81.6
1.50	360	..	..	...	99.0	83.0
2.00	380	..	..	...	132.0	80.3
2.10	380	..	..	...	98.4	84.4
3.30	390	90	96	111	99.2	79.0

The analysis of the solutions of the set of experiments, of which the above is an example, varied with the relative quantities of slag and water charged, the rate of smoke supply, and to a large extent depended also on the temperature of the gases.

The constituents of the solutions varied between the following figures:

	Minimum.	Maximum.
Fe.	0.54%	3.0%
S.	0.49%	2.9%
Cu.	0.00%	0.8%
SiO_2.	..	3.2%

The average temperature of the incoming smoke was 393° F. and that of the discharged gases 92° F. Throughout the series the volume of smoke treated varied between 90 and 235 cu. ft. per minute.

On the whole these tests were the most satisfactory as no trouble was experienced with the apparatus or in the introduction and application of different conditions.

Succeeding the experiments described, tests were instituted for the treatment of 5000 cubic feet per minute of smoke assaying 4.5 per cent. SO_2, a volume representing the total gases discharged per minute from a 35–40 ton McDougal roaster.

The apparatus used consisted of a rotating cylinder 36 feet long and 12 feet in diameter, arranged as previously described. On account of an underestimate of the charge to be carried, the foundations, running equipment and apparatus generally were designed to sustain only a fraction of the slag and water charge necessary to absorb all of the SO_2 in the smoke;

our absorptions were therefore seldom greater than 45–55 per cent. of the SO_2 in the smoke volume. For brief periods in one case we secured absorptions of 92 per cent. and 100 per cent. We never approached a satisfactory degree of elimination of the SO_2 from the smoke, except at the expense of a breakdown with this particular apparatus. The results obtained, however, were valuable as the basis for a successful design for a cylindrical apparatus.

A study of the set of results given below will show the trend of the experiments and also make clear the limitations of the apparatus used, when it is understood that the entry "Period of run—minutes" implies "Period of anxiety before smash-up—minutes."

The entry "Slag required—theoretical" is a factor derived from the analysis of the solution, in consideration of the ratio iron dissolved to sulphur absorbed. The weight of iron dissolved is multiplied by 2.7, a constant derived from the fact that the weight of slag was approximately equivalent to 2.7 times the weight of iron contained in the slag treated.

"Slag required" represents the quantity of slag which would be required per minute, to exactly neutralize the weight of SO_2 driven from the furnace per minute. It is obvious that in practice the mere presence of this figured amount would be altogether inadequate to actually neutralize the SO_2 given off minute by minute from the furnace, since the whole of the mass is not instantaneously acted on. Depending on the degree of subdivision, the constitution of the slag and other physical and mechanical factors, a slag excess of 3,000 per cent. to 10,000 per cent. is requisite to effect a complete elimination of the SO_2 from the smoke.

	1.	2.	3.	4.	5.	
Period of run—minutes....	70	57	200	280	110	
Temp. of gas, entering....	250	425	400	387	250	° F.
Temp. of gas discharge....	77	80	80	94	100	° F.
Temp. of liquor discharge	100	118	..	130	130	
Water supplied per min., lbs.	620	396	359	138	270	
Total Fe in soln., lbs.....	479	208	604	732	652	
Total S in soln., lbs.....	309	307	656	594	548	
Rate of adding slag per min.	30.0	35 3	22 3	14.2	50 0	
Slag required—theoretical per min.,....	44.3	19.4	30.8	37.8	37.0	
Total available slag charged, lbs.....	2120	2015	4470	3998	5512	
Per cent. SO_2 absorbed of total passing through apparatus.....	38.2	46.8	39.0	19.8	43.3	
Analysis:						
Milligrams Fe per 100 cc. solution.....	1008	924	1053	1897	2194	
Milligrams S per 100 cc. solution.....	710	1360	1143	1540	1837	
Milligrams Cu per 100 cc. solution.....	21.4	10.5	15.0	15.0	9.1	

By comparison of the above data it is seen that the absorption of SO_2 tends to rise as the rate of charging slag is increased. Consideration of (2) and (5) would suggest also that the absorption rises with the temperature; this indication is confirmed in other experiments not given here. In (1) the temperature is low and the absorption high; this is probably due to the high rate of water supply combined with the comparatively high rate at which the slag wool is charged.

In order to determine the practical effect of maintaining the slag excess, which had been deduced as the necessary amount to ensure complete absorption of all the SO_2 discharged from the furnace, during any period, we commenced a cylinder experiment by introducing before starting operation, 1500 lbs. of slag wool. The results were as follows:

Period of run, 10 minutes. 300 lbs. of slag added during run.	
Rate of adding slag per min., lbs....	180 (comparative
Water supplied per minute, lbs.....	1195
Per cent. SO_2 absorbed.....	100%
Milligrams Fe in 100 cc. solution.....	1260
Milligrams S in 100 cc. solution.....	1050

After ten minutes the apparatus was stopped, measurements made and samples taken. Five minutes later the apparatus was again started and operated 15 minutes, a stop being necessary at the end of that time on account of the great weight accumulated in the apparatus—principally liquor in excess of the pump capacity.

The result at the end of the second period was:

Period of run, 15 minutes.	
Rate of adding wool per min., lbs.....	100
Rate of adding water per min., lbs.....	1001
Per cent. SO_2 absorbed.....	90.2%
Milligrams Fe per 100 cc.....	908
Milligrams S per 100 cc.....	1036

The experiments stopped short of a commercial realization of the process, due to circumstances not affecting the question of smoke elimination. However, the net results of the work sufficiently established the following facts:

(1) The acid gases of smelter smoke can be effectively neutralized by means of chilled slag, with the complete elimination of flue dust from the discharge.

(2) The toxic action of the smelter vapors and gases can be controlled by converting them into constituents of harmless compounds and causing their deposit in an insoluble form on waste land.

(3) In bringing about the control of the gases in the manner stated, it is both feasible and desirable to recover copper, lead and other values contained in the slag and in the smoke.

(4) The conservation of by-products such as green vitriol, potash and soda salts, and silicic acid is possible where markets for the material are not too far removed from the smelting plant.

(5) The indirect use of sulphurous smoke in the treatment of wastes from the concentrator in the shape of slimes and tailings, is sometimes feasible. The reaction given below will suggest the general procedure:

$$Fe_2(SO_4)_3 + SO_2 + 2H_2O = 2H_2SO_4 + 2FeSO_4.$$

$$nH_2SO_4 + Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S + nH_2SO_4.$$

ELY, NEVADA.

NOTES ON A STUDY OF THE TEMPERATURE GRADIENTS OF SETTING PORTLAND CEMENT.[1]

By ALLERTON S. CUSHMAN.

The reactions that take place when hydraulic cements are tempered with water and while the mixture is hardening are not as yet understood. It is true that many theories have been advanced in regard to the hardening process or processes but more data are

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

required before much that now seems inexplicable can be understood.

Since all chemical reactions are accompanied by definite and measurable thermal changes, complete temperature records of hardening cements should yield interesting and valuable data.

It is well known that if a Portland cement clinker is ground without the addition of from 2 to 3 per cent. of calcic sulphate or gypsum to act as a restrainer it will be "flashy." By "flashy" is meant the tendency to harden very quickly, so quickly in fact that in many cases it is impossible to mold the wetted cement into a plastic mass. While this sudden hardening is going on, a considerable amount of heat is generated so that the mass feels hot to the hand. The temperature rises about 10° to 15° C., but the heat reaction lasts only a short time and after cooling no further heat reaction takes place. When, however, a Portland cement has been properly restrained by grinding with it 2 or 3 per cent. of gypsum (plaster) the conditions of thermal activity are changed in a quite extraordinary manner. On mixing a normal Portland cement with sufficient water to form a normally plastic mass, a certain amount of heat is immediately disengaged although not so much as in the case of an unplastered cement. The plastic mass soon cools down to the air temperature and generally falls somewhat below the surrounding temperature, showing that a decided cooling effect is taking place. If now the plastic mass is allowed to stand quiescent in a constant temperature chamber, nothing of moment happens for a period of from four to eight hours, if the cement be a normal standard brand. At a given time however for every mixture, a secondary heat rise begins and increases more or less rapidly to a definite maximum. After this rise is completed the cement has attained its final set and a gradual cooling takes place to the temperature of the surrounding air and nothing further happens. If an imperfect, damaged or lumpy cement is under observation the temperature gradient for the rise may show aberrations. That is to say, a sudden rise may be followed by a temporary cooling only to be followed by another rise.

The wonderful effect of a small percentage of gypsum plaster in thus controlling and regulating the temperature gradients or reactions of setting cement is little understood and indeed presents certain anomalous occurrences for our consideration, as will be shown later on.

The first successful attempt to record the temperature gradient of setting cement as far as the writer has been able to ascertain was made by Gary who used a photographic recording device which has been fully described by Burcartz.[1] The method consisted of placing the bulb of an ordinary glass thermometer in the cement paste. The whole arrangement was enclosed in a box through which a beam of light was made to impinge through a slot upon the graduated stem of the thermometer and then upon a traveling photographic film. As the mercury rose or fell the beam of light was cut by its shadow and thus a continuous temperature gradient was obtained.

[1] *Eng. Record*, Dec. 11, 1909.

The only criticism of this method that can be made is that it calls for an expensive and delicately adjusted piece of apparatus which few laboratories would care to install and in which the temperature changes cannot be watched while they are taking place. The apparatus used by the writer is simple, comparatively inexpensive and can be installed and used in any laboratory for making daily records. The apparatus is shown in Fig. 1.

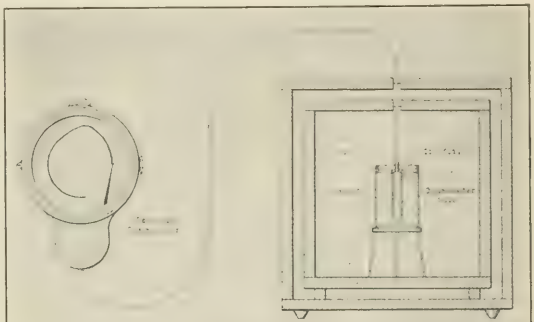
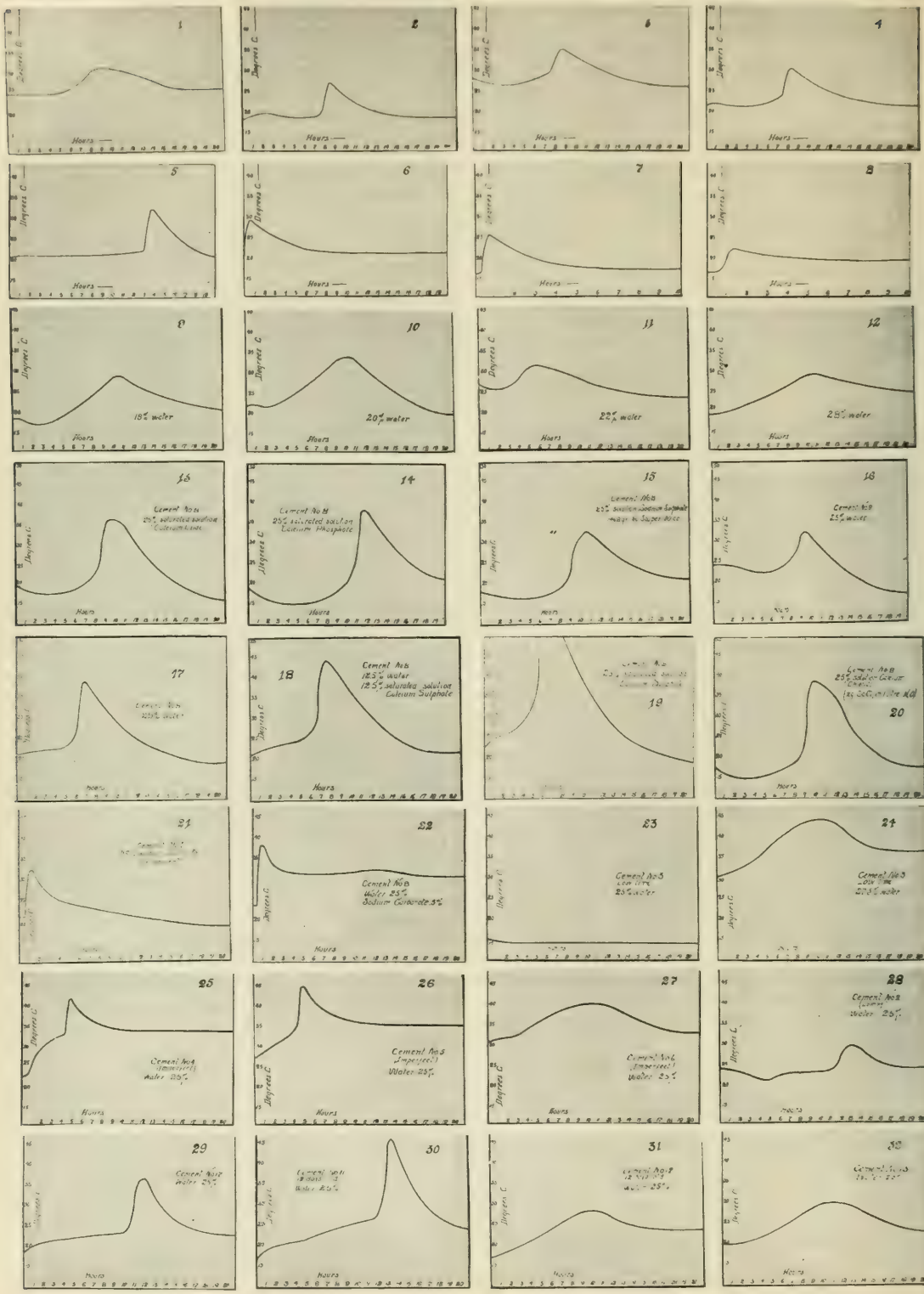


Fig. 1.

A double walled wooden box as shown in Fig. 1 is used simply to avoid any sudden changes which may take place in the laboratory temperature during a test run. An ordinary so-called "fireless cooker" such as can be bought at any kitchen supply store answers very well for this purpose. The recording thermometer is of the Tycos type and consists of a copper-plated steel tapered mercury filled bulb 9 cm. long by about 2 cm. in its maximum diameter. The bulb is connected to the recording dial by a flexible steel capillary tube. The recording dial has a range from 10° to 120° F. The recorder is fairly accurate for the middle range and is easily calibrated and adjustable.

In ordinary tests as carried out in the writer's laboratory, 1 kilogram of the neat cement is tempered with 250 cc. of water to make a homogeneous plastic paste which is packed into a No. 2 open top tin can. The thermometer bulb is not inserted until the primary heat effect (which always develops when cement is kneaded with water) is over, and the paste reaches approximately the same temperature as the calorimeter box. In the meantime the copper-plated thermometer bulb is smeared with vaseline and wrapped with several folds of fairly heavy tin foil. The object of these precautions is two-fold: (1) to guard against the "freezing" in of the bulb when the cement hardens; (2) to overcome any possible pressure on the walls of the bulb if the cement shrinks or expands during the hardening process. With 25 per cent. of water the consistency is somewhat softer than the normal, but experience has shown that the wetter mixture gives better results under the conditions of the test. When all is ready the covered bulb is pushed into the cement paste, care being taken that it is not pushed below the surface so that


1
2
3
4
5
6
7
8
9
18% water
10
20% water
11
22% water
12
28% water
13
Cement No 5
25% saturated solution
Calcium Lime
14
Cement No 4
25% saturated solution
Calcium Phosphate
15
Cement No 5
25% solution Sodium Sulphate
16
Cement No 5
25% water
17
18
Cement No 5
12.5% water
12.5% saturated solution
Calcium Sulphate
19
20
21
22
Cement No 5
Water 25%
Sodium Carbonate 5%
23
Cement No 3
Low Iron
25% water
24
Cement No 3
Low Iron
27.5% water
25
Cement No 4
(Impurest)
Water 25%
26
Cement No 5
(Impurest)
Water 25%
27
Cement No 6
(Impurest)
Water 25%
28
Cement No 2
(Lime)
Water 25%
29
Cement No 2
Water 25%
30
31
32
Degrees C
Hours

the cement can close over the shoulder of the bulb and so imprison it when hardening takes place. When these precautions are taken the apparatus gives no trouble and the bulb is easily withdrawn from the hard cement at the end of the test. The temperature gradients are usually taken for a twenty-four hour period, although this is not necessary unless the full cooling curve is desired.

In presenting these notes on the temperature gradients of setting cements, it is not the intention of the writer to draw any conclusions at this time in regard to the mechanism of the hardening reactions.

The curves obtained on the revolving scale are transferred to centigrade degrees and plotted in rectangular coördinates as is shown in curves 1–32. An inspection of the curves will show that in some cases the temperature gradients are much steeper and more sudden than in others. Curves 6, 7, 8 and 21 represent cases in which the water was simply poured on to the dry cement without previously kneading the mass to a paste. In no case of this kind is a rise in temperature noted following the final set or hardening, at about seven to eight hours.

In the cases of some brands of cement, as is shown in curves 9, 10, 11 and 12, the rise in temperature is constant and gradual to a maximum which usually occurs at about ten to eleven hours. In other cases, notably in curves 17 and 29, the rise is sharp and sudden. As both types of cement pass muster in the standard tests, it is not possible at the present time to state what the ideal temperature gradient curve for a cement should be.

That the maxima and shape of the curves is modified by the addition of various salts to the tempering water is shown in curves 13, 14, 15, 16, 17, 18, 19, 20 and 22.

Perhaps the most extraordinary curve is number 19 which shows the heating effect produced by saturating the water with calcium sulphate. In this case the temperature rose above the scale of the recording device and the test piece became uncomfortably hot to the hand. Since calcic sulphate is used as a restrainer when ground with a cement, this extraordinary effect of calcic sulphate solution is difficult to explain.

Curves 25, 26, 27 and 28 were from cements which did not stand test and had been rejected. The abnormality of these curves is at once apparent to the eye and furnishes the best argument as to the value of a study of the temperature gradient as an additional method of control in cement testing.

In conclusion, the author wishes to point out that these notes on the study of temperature gradients are offered not as data on which to establish theories but to stimulate other workers to include similar investigations in their studies of the hardening of hydraulic cements.

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COBALT DRIERS.[1]

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The cobalt compounds which are generally offered on the market to-day may be divided into two classes: In the first are cobaltous oxide, acetate, sulphate, chloride, nitrate, hydroxide, and basic carbonate. In the second class are various grades and qualities of resinates (sometimes called sylvinates), both fused and precipitated, oleates or linoleates, oleo-resinates, tungates and resino-tungates, besides some other liquid preparations composed in whole or part of the foregoing.

From the varnish manufacturer's standpoint the substances in the first division are crude materials which are utilized in the production of the compounds in the second class, and also in the preparation of some varnishes, liquid driers, drying oils, and the so-called paint oils. The materials enumerated under the second class are the result of a varnish maker's labor, and when properly made and used in mixtures to which they are adapted give very good results.

The inorganic salts of cobalt do not directly come under the scope of this paper, and thus will not be directly considered except inasmuch as their use as crude material affects the driers into whose composition they enter.

It is only within the past year that the cobalt driers have been offered to the American paint and varnish manufactureres. Up to the present time their use is not general, first, because of the very high price, and second because their use is not thoroughly understood and many experimenters have had unsatisfactory results and therefore refused to further consider the introduction of the new material. Furthermore, not all of the cobalt driers, whether liquid, paste, or solid, now offered for sale, are properly made and truly adapted to the purposes for which they are recommended. This situation in addition to unsatisfactory results obtained by some of those experimenting, would naturally have a retarding effect on the introduction of a new type of material.

The salts of cobalt which are at our disposal in commercial quantities, are all of the cobaltous or divalent type. It has been found that although they can be readily used in the manufacture of driers and worked like the various compounds of manganese, lead, zinc, calcium, aluminum, etc., the organic compounds formed, which are the basis and active principles of the so-called driers, are not efficient while in the cobaltous state. The cobaltic combinations, however, are very active driers, and it is for the formation of trivalent cobalt compounds that we strive in the making of driers. This transformation can be effected in several ways. By blowing cold, heated, or ozonized air through the hot cobaltous drier stock, or by the introduction of liquid or solid oxidizing agents. The use of cold or even heated air is a very long and tedious operation if carried out to the extent to which it is necessary in order to get the maximum strength in the drier, and greatly adds to the cost of an already expensive material. The use of the liquid or solid oxidizers can be carried out successfully and in a comparatively short time, although even when great care is exercised the batch of material is in danger of catching fire.

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

Since driers are used in a number of industries in which drying oils form part of the material produced, and since the operating methods of the various manufacturers are widely divergent, the siccatives or driers adapted to each will in many instances show widely different characteristics, not merely in form but also in composition.

Since the paint manufacturer and also the practical painter who mixes his own paints from paste colors and raw or treated oil, are the principal consumers of what are generally known as driers, the materials adapted for their use may be first considered. The driers will, in practically all instances, be in the liquid state, either very fluid, of heavy consistency or of a semi-paste nature. In composition, they will mostly consist of resinates, tungates, oleates, or linoleates, or combinations of the three. For the drying of linseed oil, when the proper driers are selected, little or nothing can be asked in addition to those known at present. When the general lead, manganese and other prevalent metallic driers are well chosen, raw linseed oil can without any difficulty be made to dry by the addition of from 5 to 10 per cent. or even less, the time of drying under average weather conditions being from 10 to 24 hours. By the use of cobalt driers, the same drying effect can be obtained when only from 1 to 3 per cent. of a liquid drier is used. I am not yet prepared to say positively what the ultimate effect of cobalt driers is upon paint films, but from my experiments I am led to believe that cobalt has not the harmful progressive oxidizing action that some of the usual manganese lead compounds have. It has also been noticed that although a cobalt drier may be fairly dark in color, it will not have as darkening an effect as one of the usual driers of like color would have upon a white paint. The cobalt driers likewise show the same phenomena as some of the others when used in excessive amount; that is, although the paint film will set up well in the usual time, the drying action apparently reverses and the film remains tacky.

The terms applied to liquid driers are often uncertain and apt to be misleading. There are no general standards for strength or consistency, and, it must be admitted, many of the materials found on the market contain more volatile thinners than is conducive to obtaining a maximum drying effect with a minimum quantity of drier.

The value of the cobalt specialties depends not on their power to dry linseed oil, but on their ability to make the lower priced semi-drying oils act like it.

Soya, fish, and even corn and cottonseed oil are adaptable for use in paint, and when correctly treated increase its durability. Dr. Maximilian Toch has published the results of his extensive research and experimental work with both fish and soya oils, and there describes the types of driers suitable for them.

In the making of waterproof fabrics, insulating coatings, etc., both liquid and solid driers are used. In the linoleum, oilcloth, patent leather, artificial leather and similar industries, the semi-liquid, paste, and solid driers are in demand since for these products the manufacturers cook the oils and varnishes in their own factories.

The paste and solid driers must essentially be considered under the caption of crude materials because they must be churned or cooked in the oils or varnishes in which they are used.

The methods of making both solid and liquid driers are in general similar in the first stage of the process, and thus may be described under the same headings.

RESINATE OF COBALT, PRECIPITATED AND FUSED.

This is correctly made by saponifying rosin or colophony with caustic soda or sodium carbonate, care being taken to avoid an excess of the reagent, and then precipitating with a solution of some salt of cobalt. The chloride or sulphate serve best for this purpose. The precipitated resinate, or as it is sometimes called, rosinate or sylvinate, must then be thoroughly washed and then pressed and dried. This will yield a pinkish, fairly fluffy powder when ground, which will readily dissolve in oil at a low temperature. The fused variety is made by melting the dried resinate in a kettle and then pouring into cooling pans. The operation is performed more rapidly by taking the cakes from the presses and driving off the water and fusing in one operation.

COBALT OLEATES OR LINOLEATES.

The basis of this class is generally linseed oil, although walnut, perilla, soya, and some other oils may be used. The oil is thoroughly saponified with caustic soda and, like the resinate, precipitated with a salt of cobalt. The material is then carefully washed and pressed. It may be melted to form a dark viscous heavy fluid.

Several samples of cobalt linoleate which I examined consisted of bodied linseed in which small amounts of inorganic cobalt salts had been dissolved. Another was of the same order with the addition of volatile solvents.

True linoleate of cobalt, when fused with varnish gums and dissolved in volatile oils, yields an excellent drier.

OLEO-RESINATES.

This type of drier is made by melting together the precipitated resinate and linoleate, sometimes with the further addition of fused fossil gum-resins.

TUNGATE OF COBALT.

Like the linoleates, the tungate of cobalt is made by saponifying pure China wood oil (tung oil) with caustic soda, care being taken to avoid excess of caustic, and then precipitating with a salt of cobalt. The tungate is then washed thoroughly, pressed and generally dried and fused. Great care is necessary in the preparation of a tungate since it oxidizes very rapidly, and the oxidized material is useless.

Like the linoleate of cobalt, the tungate may be fused with the resinate to form what may be called a resino-tungate.

In general, the foregoing substances are incorporated in oils by means of heat, the combining temperature being between 300° and 500° F. The amount necessary will vary from about $^1/_2$ per cent. to 5 per

cent. In order to make *liquid driers*, the paste or solid driers can be melted alone or in combination with gum-resins, bodied linseed oil, or both, and then thinned to liquid consistency with volatile oils.

Among other cobalt salts, some of the chemical manufacturers offer the acetate, with directions for its use as a drier. All agree that between two- and four-tenths of one per cent. are necessary to dry linseed oil. The oil should be at a temperature between 300° and 400° F., and be carefully stirred until all the salt is dissolved. Soya and China wood oil may be similarly manipulated.

It is still a little too soon to make a positive statement as to how oils thus treated with the acetate withstand wear and exposure

Cobalt oxide, like the acetate, can be directly added to oil during boiling. It however dissolves slowly and necessitates heating to high temperature; the resulting product is also very dark, and mostly consists only of bodied oil. Rosin also will directly combine with cobalt compounds on heating together in a suitable kettle or container. The product possesses a number of objectionable features. It still is mostly unchanged rosin, has become much darker and lost considerably in weight due to volatilization. I have tried the effect on oils of quite a number of cobalt compounds, but found none equal in efficiency to those described in the foregoing.

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THE DEVELOPMENT OF HYDROSULPHITES IN THEIR RELATION TO MODERN DYESTUFFS.[1]

By PHILIP S. CLARKSON.

In 1869 when Schuetzenberger first made sodium hydrosulphite and in 1872 when he, together with Lalande, applied it to the preparation of indigo-white and introduced a vat for indigo dyeing based on its use, a basic foundation was laid for the practical application to the fibre of the latest and the most desirable group of synthetic dyestuffs. These are now known technically as "vat colors" but some better term should be applied to them than one derived from the large vats or dye vessels necessary on account of the quantity of sediment in the old style method of indigo dyeing. As is well known, these products are insoluble in water and require reduction, generally in an alkaline solution, to render them soluble and suitable for use in the dye kettle. The old methods of fermentation, etc., used with indigo are not applicable here and the hydrosulphites are found to be the most satisfactory agents, being most energetic in reducing action, and in the form of their sodium salts giving no insoluble combinations with the dyestuffs.

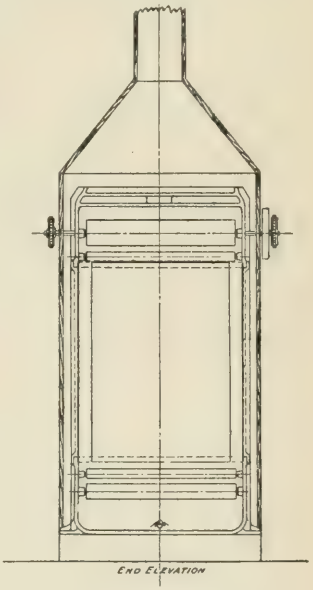
Before the discovery and invention of the now large group of vat dyestuffs, the use of hydrosulphite in dyeing was small, and the improvement in manufacture of hydrosulphites not marked, but coincident with the discovery of new coloring matters suitable for use in vat dyeing came new interest in the use of hydrosulphites as discharging agents in calico printing.

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

This led to the discovery of the formation of stable compounds with formaldehyde for which the first American patent appeared in 1904[1] followed by that for the production of pure sodium hydrosulphite powder in 1905,[2] that for sodium formaldehyde sulphoxylate in the same year and finally the two zinc salts in the year 1911.

These may be said to represent the products now in commercial use, the pure sodium hydrosulphite powder ($Na_2S_2O_4$) representing the products used for dyeing, the formaldehyde compounds those used for printing and for discharging. These are as follows:

Sodium-formaldehyde-sulphoxylate, $NaSO_2.CH_2O + 2H_2O$, which is commercially known as hydrosulphite N F conc., Rongalite C and hyraldite C extra, according to the maker. This is the compound of especial interest to the calico printers.



Di-zinc-formaldehyde sulphoxylate,[3] $ZnSO_2CH_2O$, is known to the trade as hydrosulphite A Z, decrolin or hyraldite Z. This is used only for stripping or removing dyestuffs from dyed materials.

Mono-zinc-formaldehyde sulphoxylate,[4] $Zn(HSO_2CH_2O)_2$, which is hydrosulphite A Z soluble conc. This is used for the same purpose as the di-zinc salt, but is more effective and is soluble in water.

The other commercial marks represent mixtures with various substances for special purposes.

Practical Applications.—These comprise dyeing, printing, discharge-printing on dyed materials, and stripping or the removal of dyestuffs and coloring matters from previously dyed material. The dyestuffs which require the use of hydrosulphites are as commonly classed: indigo and substituted indigoes, usually halogen substitution for hydrogen; indigoids, those having the molecular construction of indigo but having other replacements; and anthracene compounds.

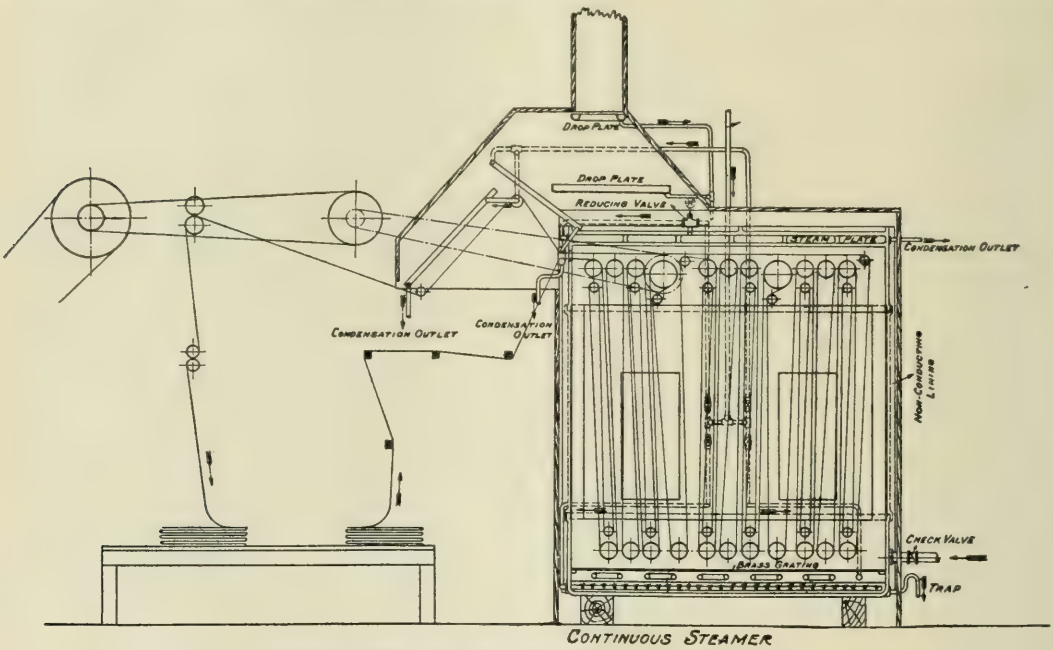
Dyeing.—The method of application for all these classes of dyestuffs is practically the same; the dyestuff is reduced with 1½ times to twice the amount of sodium hydrosulphite in the presence of alkali to dissolve the leuco compound formed. This reduced dyestuff is then applied to the fibre in the well known manner and the color finally developed by oxidation. Various assistants are added to secure technically

[1] U. S. Patent No. 769,593, Des Camp.
[2] U. S. Patent No. 793,559, Bazlen and Wohlfart.
[3] *Ber. d. chem. Ges.*, **1909**, p. 4657.
[4] B. Fran., 435,260.

perfect results. The shades obtained are generally speaking much in advance of any previously known in regard to fastness to all injurious influences combined with brilliancy of shade.

Printing.—It is in this branch of the art of coloring that the most marked change has taken place. Previous to the development of the application of vat colors in this industry, the dyer was far ahead of the printer in the production of shades of extreme fastness. Especially the manufacturing and finishing process depends on the production of insoluble color lakes in the process of coloring. The hydrosulphite-vat color process of printing provides this nearly in perfection. The required installation of machinery is not extensive, the success or failure of the operation depending mainly on the proper construction and condition of the steamer, preferably a Mather-Platt. This must be arranged so that all access of air is excluded and suitable steam plates provided for heating so that the interior is at all times at a temperature of 102°–104° C. (see figure). With proper conditions here and the usual care in making up the print colors failure is not to be anticipated. The present application of the vat colors in the printing process depends on the use of sodium-formaldehyde-sulphoxylate. This is stable at ordinary temperatures and enables the pastes to be made up without difficulty, and the prints from the machine are uniform throughout the length. On steaming, the sulphoxylate is liberated and at once reduces the dyestuff to its soluble condition in which it combines with the fiber. After steaming, the material is treated with either soap or oxidizing agents which fully develop the color in an insoluble condition. By the proper selection of dyestuffs the printer can furnish shades which can be guaranteed as fast to light, washing, wearing and other injurious influences, in fact almost that the color will last longer than the fibre. This condition has undoubtedly been brought about by the discovery and perfection of the hydrosulphite-formaldehyde compounds. This is the present state of the direct printing industry; now the printer is ahead of the dyer for he can work more economically and the results are in every way satisfactory to the consumer. One of the very apparent results is "laundry-proof shirts for one dollar."

The method of discharging azo colors by the use of these salts has been used for sometime and cannot be said to have been very recently developed—only improved by the use of sodium-formaldehyde-sulphoxylate in place of the zinc-dust-bisulphite mixtures of the original formulas.



Continuous Steamer for Indigo Discharges and Vat-color Prints.

But the use of formaldehyde-sulphoxylate for discharging white patterns on material dyed with indigo is the most recent and the most notable advance in the printing industry brought about by the use of hydrosulphites. It has long been known, and use has been made of the fact that oxidizing agents would destroy indigo blue and render it colorless and all the discharge printing on indigo has been based on this. The great disadvantage has been, however, that these agents also acted on the cotton fiber and the formation of oxycellulose with material loss of strength has occurred. By the use of reducing agents this could be avoided but the difficulty was to remove the indigo-white produced in the pattern before it became re-oxidized.

In 1907 one of the foreign manufacturers of indigo suggested the use of anthraquinones in the printing

paste with sodium formaldehyde sulphoxylate. This rendered the discharge more energetic and also hindered the reoxidation, but it was necessary to handle the material very quickly to avoid tarnishing the whites. The usual conditions of the printing rooms rendered the production of uniform results almost impossible and little practical use was made of the process in this country.

However, in the last two years a notable advance has been made owing to the discovery that certain bases of the substituted ammonium type would combine with indigo white to form stable compounds which do not oxidize in the air. Further experiments proved that this property was characteristic of compounds of certain tertiary bases with benzyl chloride, its homologues and analogous bodies and their substitution products. In the presence of zinc oxide desirable reddish to yellow shades can be obtained by this method.

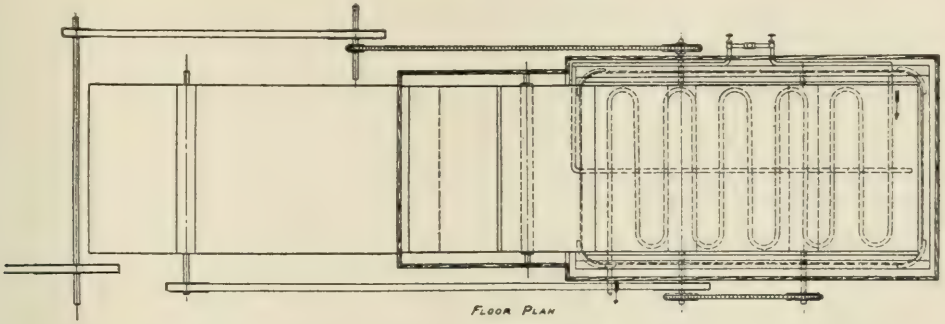
But in order to obtain white discharges the compounds obtained in the discharge process had to be made readily soluble. It was found that this could be done by the substitution of a sulphonic group in the benzyl nucleus. The yellow compound obtained by using a substance of this nature in the formaldehyde sulphoxylate discharge paste is readily soluble in alkalies and being easily removed from the material leaves the patterns clear.

Thus the problem of satisfactory indigo discharges was solved. For certain considerations the discharge material is not sold as such but in combination with sodium formaldehyde sulphoxylate as hydrosulphite C L or rongalite C L, according to the maker.

The practical method of handling is simple. The discharge pastes are made up with 20 per cent. of the sulphoxylate discharge compound, 8 per cent. zinc oxide, 4 per cent. anthraquinone, 30 per cent. paste, with suitable thickening. The material is printed, dried, steamed in the before described steamer for 3–5 minutes at 100°–103° C., washed in hot water, then passed through an alkaline bath, washed and dried. In this process, the pastes are perfectly stable and after printing and steaming the material can be left indefinitely before clearing. The writer kept a piece for two months before clearing and the resulting whites were perfect.

The process has been adopted by the largest indigo printers in this country. In spite of the fact of the higher cost the commercial product now represents the standard of indigo prints. The gain to consumers is in the same proportion: for the strength of the material is not affected and after the garments are washed three times the whites are no longer holes but remain the original material.

The zinc-formaldehyde-hydrosulphites are used solely for removing the dyestuff and colors from previously dyed material and have little interest for the phase of the subject under consideration. Their great advantage lies in the fact that the strength of the fiber is not affected.



FLOOR PLAN

The increase in the use of hydrosulphites and the formaldehyde compounds has been most marked and the probable consumption in the textile industry in the United States for the year 1911 was not far from one million pounds.

NEW YORK CITY.

THE EFFECT OF "LIME-SULPHUR" SPRAY MANUFACTURE ON THE EYESIGHT.[1]

By JAMES R. WITHROW.

About two years ago, the writer was called upon to take charge of the installing of a "Lime-sulphur" department for a manufacturer engaged in other lines of chemical manufacturing. Preliminary to starting industrial experimentation, a very thorough laboratory study had been carried out by the manufacturer's regular chemist. This work reviewed in a most capable manner about all the recommendations of recent chemical and experiment station literature concerning "lime-sulphur" preparation. As a result of this work a formula was evolved, which was used as a basis for manufacturing experiments. The laboratory experiments themselves were never made in larger than five-gallon apparatus. The writer witnessed, from time to time, these experiments or portions of them and at no time noticed anything causing discomfort. The laboratory assistant, who did most of the experimental work for the company's chemist and was constantly in contact with the material and its fumes, never noticed any effect or discomfort at any stage of the laboratory work, which extended through several months. To be sure, there was the ever present odor of hydrogen sulphide or at least a similar odor. This was never offensively strong. At no time was it

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

so noticeable as to compel enforced ventilation.

The writer's business was to accept the work as completed in the laboratory and transfer it to factory operation. The first factory experimental runs were made on about a 12-barrel scale. These experimental cooks were made to get factory scale data for construction work and also to uncover any unforeseen operation difficulties. The product had varying specific gravity from 45° to 32° Bé., depending on the purpose of the experiment. The final solution of calcium polysulphide or so-called "lime-sulphur" contained about 25 per cent. sulphur and about the equivalent of 10 per cent. calcium oxide, when the specific gravity was about 33° Bé. Twelve barrels of this product therefore would contain 1625 pounds of sulphur and the equivalent of 650 pounds of lime.

The first few cooks aroused no comment from employees about the building, which was a large one of four stories, beyond what would come from persons unaccustomed to hydrogen sulphide. In the course of the next week or two, however, the weather had become quite cold and the normal ventilation by means of the windows was much diminished. Again no particular effect was noticed at first. The "cook" digester was a steam jacketed cylindrical tank roughly 5′ × 5′ and supplied with a cover and a small ventilating pipe. This pipe was inadequate for proper ventilation of tank and would have been useless anyway, for the top of the "cook" tank was usually open during the experimental runs for observation purposes. The man in charge of the cooks usually stationed himself at the opening to become familiar with boiling conditions within the tank during the various runs under different conditions.

Within a cook or two, after the windows were closed to diminish the cold conditions, the man in charge of the cook became aware of a smarting sensation in and around the eyes. The eyelids became red. The writer was constantly about the tank, but was only occasionally at the tank opening and felt little or no discomfort, though there was a slight burning feeling about the eyes. The room became partially filled with condensed steam at times and finally about 8.00 P.M., during a slightly prolonged run, the writer noticed that the amount of vapor in the room was greater than usual and that the incandescent electric lights had a halo of some eighteen inches in diameter when viewed through the fog: the halo tended to have rainbow colors. An hour or two afterwards, the writer found the same conditions as to fog and halo to exist in his room in his hotel and concluded that his eyesight was affected. Cold water was applied liberally and he turned into bed and went to sleep at once. In the morning the blurred eyesight was about as bad as the evening before. The foreman, who stood at the opening of the cook tank, had gone home at the end of the run at the time the writer did. He was unable to report for work next day. His eyes were much inflamed and were too sensitive to light to open them. He said they pained and felt gritty under the eyelids. He was back at work again in a couple of days. In the case of the writer, with the liberal use of saturated boric acid solution, the blurred vision gradually returned to normal during the course of a week's absence from the manufacturing operation. There was a recurrence of the blurred effect at another time, which rendered vision almost impossible, but it rapidly wore off and at no time was there any pain. The foreman never again had an attack after his initial experience. None of the workmen were affected after proper precautions were taken.

At one time however, when a batch was being concentrated by boiling down, the cover was thrown open to expedite evaporation. In the same room some distance away, two workmen were barreling off finished product. Both the foreman and myself were actively engaged about the cook tank and were practically unaffected. Of the two workmen mentioned however, the thin one was very much affected and said he suffered agony all night and next day, while the corpulent one was entirely unaffected. Other workmen were in and out during the cook but none were affected. The one of the two mentioned above as unaffected has, since starting regular operation in the new plant and in fact during the rest of the experimental runs, been in active charge of the "cooks" and has never become affected, beyond possibly a slight reddening of the eyes.

No one at all has been affected in anyway since the new plant was installed with its ample facilities for ventilation. Inquiry directed to other manufacturers disclosed similar experiences. One manufacturer's experience was so bad that he at once knocked one side out of his cooking room. This is undoubtedly effective, but from the writer's experience unnecessary. All that is required is a hood over the cook tank, which will carry all vapors out doors, and a "cook" room which is high ceilinged and reasonably well ventilated. Providentially the copious evolution of steam has caused most plants to provide hood-covered tanks, thus avoiding the unexpected trouble we are discussing.

A search of the literature of "lime-sulfur" available to the writer found no mention of the effect of the eyes. The suggested reactions to explain the action of sulfur on calcium hydroxide and water, varied as they were, gave no clue to what might have been the body which gave rise to the trouble. During a subsequent study of polysulfide literature in general, however, it was found that Bloch and his pupils[1] had prepared polysulfides of hydrogen of the formulas H_2S_3 and H_2S_2. The latter is formed by heating the former and is easily volatile. The fumes of these polysulfides are said to have a penetrating disagreeable odor and their vapors attack the mucous membranes. Thorpe says their vapors attack the eyes.[2] They are decomposed by alkalies and therefore would not exist very long in the lime-sulfur cook, but if they were being given off in mere traces, continuous exposure to such fumes would naturally cause discomfort.

Hydrogen sulfide itself, however, may have been the cause of the trouble. It has been shown to be a

[1] *Ber. d. chem. Ges.*, **41**, 1961; *Am. Chem. J.*, **41**, 155.
[2] *Dict. Applied Chem.*, **3**, 699 (1893).

product of the evaporation of a solution of calcium polysulfides.[1] Hydrogen sulfide could not likely have been the cause, unless the symptoms of H_2S poisoning recorded are the effects of only sudden or brief exposure to large amounts of the gas and that prolonged exposure to dilute H_2S would cause a different series of violent symptoms. This latter assumption does not appear probable for in such cases where H_2S was permitted in the atmosphere of laboratories in small amounts, the *usual* symptoms, only not so pronounced, were the result. The only recorded symptom of hydrogen sulfide poisoning observed in the cases under discussion was the occasional occurrence of headache. This was to be expected, since hydrogen sulfide was itself being evolved to some extent.

It should be mentioned, however, that K. B. Lehmann[2] mentions cases where "intense irritation of eyes, nose and throat" occurred within five to eight minutes of exposure to a concentration of 0.3 per thousand of hydrogen sulfide, but no affection of the sight is mentioned even in this extreme case. In long exposure to lower concentrations, such as would correspond with the case of hours of exposure in lime-sulfur cooking, the action recorded is on the respiratory tract. These symptons appeared entirely absent in the lime-sulfur cases as also were all the other common symptoms (except headache), such as muscular weakness, etc. A tendency to conjunctivitis, a symptom of chronic hydrogen sulfide poisoning, may have been present in the case of the man in charge of the cooks. He was the man, however, whose eyesight itself was never affected. The writer has suffered at other times in the last six years, most of the symptoms of slow hydrogen-sulfide poisoning, due to inadequately ventilated, over-crowded and poorly arranged university laboratories, but the symptoms in the lime-sulfur experience were quite different. In fact the usual muscular weakness and general depression as caused by hydrogen sulfide were not experienced at all in the lime-sulfur manufacture. It should be mentioned also, that the writer has been informed that attendants at "sulphur" baths have had their eyesight temporarily affected in a similar fashion. Volatile polysulphides may be present in this case also, although they have not been proven to the writer's knowledge to be present in either case. This would be an interesting point for some favorably situated person to develop.

It seemed possible therefore that these hydrogen polysulphides might have been the cause of the action on the eyesight of the vapors from the boiling of a mixture of sulphur, lime and water.

It may be stated at this point that this indication of the presence of hydrogen polysulphide in the vapors of the lime-sulphur cooks might have an influence upon the solution of the problem of the actual reactions involved in lime-sulphur preparations, a mooted question at the present time. The trouble with the eyesight always came when a batch was being concentrated by evaporation before filtration and not during ordinary cooks.

[1] Divers, *J. Chem. Soc.*, **1884**, p. 284.

[2] Arch. F. Hygiene, Bd. XIV, 1892, 135; Blyth, "Poisons, Their Effects and Detection," 3rd. Ed., C. Griffin and Co., London, p. 73.

It seemed worth while to record these facts as a warning, at least, as to the serious dangers of lime-sulphur manufacture in the absence of adequate ventilation. This is all the more necessary since it is probable that attention has not already been frequently called to the matter, because ordinary ventilation precautions only, are necessary to avoid all trouble, and therefore the average manufacturer has not had the experience or it has appeared so seldom that the isolated affections of a workman now and again may have been attributed to something else. It is worth noting also because the mere occurrence of a cold spell of weather gave the opportunity of experiencing this difficulty possible in lime-sulphur manufacture, so that otherwise it might never have occurred at this plant or only in such isolated cases as to destroy any connection between cause and effect.

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PHENOL-FORMALDEHYDE CONDENSATION PRODUCTS.[1]

By L. H. Baekeland.

The resinous or amorphous products resulting from the action of phenolic bodies upon formaldehyde have lately attracted considerable attention on account of their rapidly increasing applications for industrial purposes.[2]

It is questionable whether this general designation of "condensation products of phenols and formaldehyde" should be maintained much longer. Indeed, it is well known that these products can be obtained without the use of so-called formaldehyde. In fact, the first condensation products thus described were produced without the use of formaldehyde,[3] and it is generally accepted that other methylene compounds, for instance, methylal, trioxymethylen, hexamethylentetramin, etc., can replace formaldehyde in this reaction. The fact that hexamethylentetramin can suitably replace formaldehyde in the formation of the infusible phenolic condensation products was published as far back as December 31, 1907, by Lebach.[4]

Lately, I have succeeded in producing fusible resinous condensation products identical with those described by Blumer, DeLaire, etc.,[5] by introducing a mixture of salicylic acid and an inorganic acid in the cathode compartment of an electrolytic cell in which sodium chloride is electrolyzed, a mercury cathode being used. According to the well known reaction of Kolbe, the carboxyl group of salicylic acid is introduced by reacting with CO_2 on phenolate of sodium, so that we have here an example of the possibility of introducing indirectly the methylene group as CO_2, then reducing the carboxyl group by means of nascent hydrogen. A similar observation

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

[2] Baekeland, This Journal, **1**, No. 3, 149 (1909); No. 8, 545 (1909); **3**, No. 12, 932 (1911).

[3] *Ber.*, **5**, 1905; **19**, 2009, 3004; **25**, 3477; **27**, 2411.

[4] Knoll patent, Belgium, No. 204,811, December 31, 1907. Ditto. Wetter (Knoll) British patent, No. 28,009, 1907, owned by the Bakelite Gesellschaft of Berlin.

[5] Baekeland, This Journal, **1**, 545 (1909).

has already been recorded by Velden,[1] who expected to get oxybenzyl-alcohol by reducing salicylic acid but obtained the corresponding saliretin-body resulting from the dehydration of phenol alcohol.

However, the designation "phenol-formaldehyde condensation products" has been so generally used, that for a while at least, we shall have to submit to it as a matter of routine.

In the same way, we are erroneously designating as "formaldehyde" a commercial aqueous solution containing some real formaldehyde or methylen-oxide, CH_2O with much methylen-glycol, methylal, trioxymethylens, hydrates of trioxymethylens, other polyoxymethylens, etc., all compounds of methylen of which the technical value is equivalent in this reaction to that of true formaldehyde.[2]

The direct relationship of the resinous condensation products to phenol alcohols or their anhydrides seems now pretty well established. The so-called fusible soluble resinous condensation products are merely varieties of the saliretins,[3] and all these products differ from each other only by greater or lesser fusibility, solubility, or hardness, and each of these properties can be modified at will. Furthermore, we have the means at hand of producing all these bodies directly from phenol alcohols.[4]

The formation of ortho- and para-oxybenzyl-alcohol, or their homologs, by Manasse and Lederer, is sufficiently well known;[5] this process consists in the direct action of one molecule of phenol on one molecule of formaldehyde in presence of one molecule of NaOH under special conditions.

Then DeLaire[6] showed that these same phenol-alcohols can be transformed industrially, by dehydration, into fusible resins or saliretin products suitable for commercial purposes in place of shellac, copal, or other natural resins. In that process, it is not necessary to first produce the phenol alcohol in pure form, and the two reactions can be carried out practically at the same time, so that the phenol alcohol is dehydrated to saliretin resins as soon as it forms.

This is accomplished more directly by reacting with phenol on formaldehyde in presence of an acid,[7] provided the reaction be carried out under suitable conditions. One of the required conditions is that the phenol should be in excess so as to avoid the formation of variable amounts of infusible and insoluble products. A fusible soluble saliretin can thus easily be prepared which has all the appearances of a resin; it melts if heated and solidifies by cooling; it is soluble in alcohol and acetone; it can be maintained in fusible condition for very long periods without becoming infusible or insoluble, provided heating be carried on below certain temperatures, and provided the excess of phenol be not removed. This fusible resin and its preparation has been described by Blumer, and DeLaire as a "shellac substitute," or "resin substitute;"[1] by Baekeland, who calls it "Novolak;"[2] and lately again by Aylsworth, who calls it "phenol resin,"[3] In whatever way it be obtained, whether by using a phenol alcohol (DeLaire, Baekeland), whether by starting from phenol and formaldehyde in the presence of oxy-acids (Blumer), or in the presence of mineral acids (DeLaire, Thurlow, Bayer), or by the action of phenol on formaldehyde without adding condensing agents (Story)[4] or (Aylsworth)[1] the product is absolutely the same in its chemical and physical properties. Its melting point or fusibility may be modified at will by varying the amount of free phenolic body. This free phenol exists in solid solution in the mass and can be eliminated by merely physical methods; by the partial elimination of this free phenol, the fusibility and the solubility of the resin are decreased. The last traces of free phenol cling tenaciously to these saliretin resins; so much, indeed, that at one time, I was inclined to believe that this small amount of phenol was chemically combined. Indeed, the last traces of phenol cannot be expelled by heating at the lower melting temperatures of the product. There is nothing strange in this, if we take into consideration that phenol itself has a relatively high boiling point, and we know of numerous examples where colloids retain, physically, small amounts of other bodies which form therewith colloidal solid solutions. As long as there is some excess of phenol present in the saliretin, it is possible to maintain the mass in fusion for a practically indefinite time, provided the temperature be not raised too high. Pure saliretin, containing no excess of phenol, may be kept in fusion for some time, but after a while it polymerizes and becomes less fusible until finally it changes into some infusible product. However, it should be noted right here that this latter product, although it is infusible, does not possess the maximum mechanical strength nor hardness, nor general chemical and physical resistivity, of those other polymerized infusible products, of which I will speak later on, and which are obtained by reacting with a sufficiently larger amount of formaldehyde, or equivalent methylen compounds, and which have been designated as Bakelite C.

It is possible to expel the slight excess of phenol which lends special fusibility to the so-called fusible resins; this can be accomplished whether these resins be called "shellac substitutes," "Novolak," or "phenol resins," or whether they be made directly from phenol alcohols, or from phenol and formaldehyde with or

[1] Velden, *J. prakt Chemie*, [2] **15,** 164; *Jahresbericht*, **1877,** 337.

[2] Raikov, *Chem. Ztg.*, **26,** 135; **12,** 11 (1901). Kekulé, *Ber.*, **25,** 2435. Harries, *Ber.*, **34,** 635; *Compt. rend.*, **124,** 1454; *Bull. soc. chim.*, **17,** 849. F. Auerback, also Auerbach and Barschall, *Arb. kais. Gesundh.* Band, 22, Heft 3 and Band 27, Heft 1. Verlag Julius Springer, Berlin.

[3] Beilstein, *Organ. Chemie*, **2,** 1109 (1896). R. Piria, *Ann. Chem.*, **48,** 75; **56,** 37; **81,** 245; **96,** 357. Moitessier, *Jahresbericht*, **1886,** 676. K. Kraut, *Ann. Chem.*, **156,** 123. Gerhardt, *Ann. Chim. Phys.*, [3] **7,** 215. F. Beilstein and F. Seelheim, *Ann. Chem.*, **117,** 83. C. Schotten, *Ber.*, **1878,** 784.

[4] Baekeland, **1,** No. 8, 545 (1909).

[5] *J. prakt. Chem.*, [2] **50,** 224. *Ber.*, **1894,** 2409–2411. D. R. P. Bayer, 85,588; U. S. P. Manasse, 526,786, 1894.

[6] DeLaire, British Patent 15,517, 1905; D. R. P. 189,262.

[7] Blumer, British Pat. 6,823, 1903; 12,880, 1902. DeLaire, French Patent 361,539. Wetter (Knoll), British Patent, 28,009, 1907. Knoll, French Patent 395, 657; Bayer, D. R. P. 237,786; D. R. P. 201,261; British Patent, 26,317, 1907, etc.

[1] *Loc. cit.*

[2] THIS JOURNAL, **1909,** 545.

[3] U. S. Patent 1,029,737.

[4] Austrian Patent 30,844, page 2, lines 17–20.

without acid condensing agents. Indeed, plain heating at 300° C to 350° C. or better, heating *in vacuo*, or in a current of an inert gas, like nitrogen, easily expels the free phenol, and produces infusibility. The same result is readily obtained by entraining the free phenol by blowing superheated steam through the molten resinous mass.

These facts are corroborating proofs to others which establish clearly the saliretin-nature of these fusible products, and demonstrate their relationship to the phenol alcohols from which they are derived. If these fusible resins are prepared directly from phenol and formaldehyde, the preliminary formation of phenol alcohol may escape our notice, because by the action of heat on the mixture, especially in presence of acid bodies, the phenol alcohols are rapidly dehydrated to saliretin products. But it is quite possible to demonstrate their presence, and my assistant, Dr. A. H. Gotthelf, while preparing fusible resinous condensation products, by boiling a mixture of phenol and formaldehyde, acidulated by means of HCl, has been able to extract from this mixture well defined crystals of oxybenzyl-alcohol before the heat had accomplished its resinifying action.

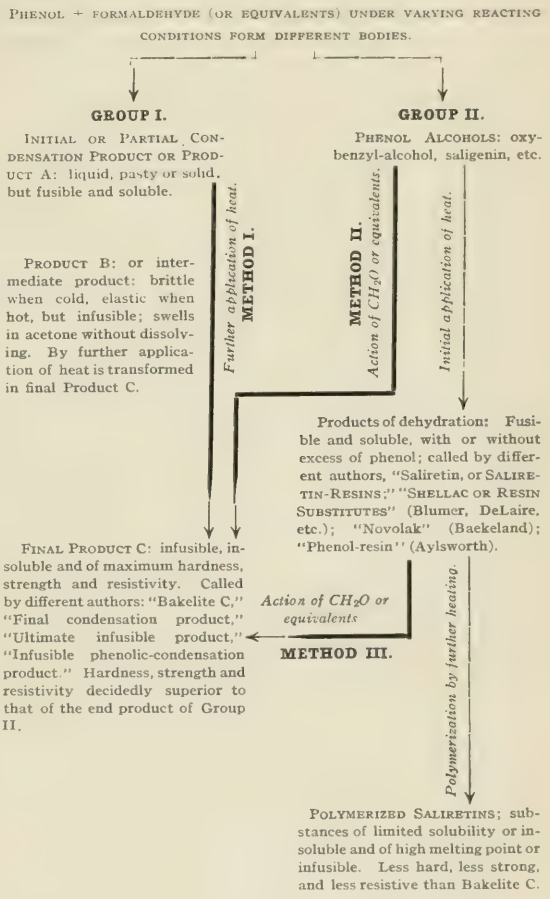
It is self-evident that as soon as high temperatures are applied to such mixtures, the formed phenol alcohol will quickly undergo resinification, because the phenol alcohol will be dehydrated to a saliretin product as soon as it is formed.

If there is an excess of phenol present, or if the formaldehyde reacts in insufficient proportions, which amounts to the same thing, a fusible saliretin will be the result.

In the absence of an excess of phenol, but using however, a restricted amount of formaldehyde or other methylen compound, a polymerized infusible saliretin will be produced.

But whenever we succeed *in bringing into reaction a sufficient amount of formaldehyde* or its equivalent, then a much harder, much stronger and more resistive infusible body than an infusible saliretin, will be formed, and this body of maximum strength and resistivity is identical with Bakelite C.

If we first produce the pure crystalline phenol alcohol, containing no excess of phenol, for instance crystalline saligenin or oxybenzyl-alcohol, and if we heat it gently, it will simply dehydrate and be transformed into a fusible mass which on cooling solidifies to a resinous product—a fusible saliretin resin. The latter submitted to the further action of heat polymerizes and becomes an infusible, insoluble saliretin. This polymerization is facilitated by the presence of small amounts of catalyzers, for instance, hydrochloric acid. The presence of an excess of phenol retards polymerization, hence the infusibility induced by polymerization will be retarded, and this until in some way or another the excess of phenol has been expelled. The infusible polymerized saliretin obtained by heating phenol alcohols containing no free phenol, or by heating fusible saliretin containing no free phenol, is insoluble in alcohol, but swells in acetone; it softens decidedly on heating, although it is no longer fusible. Longer heating does not harden it further, nor make it more resistive. It is harder, stronger, and more resistant to physical and chemical agents than the fusible saliretin from which it is derived; in this respect, it surpasses even more the soluble fusible resins described by Blumer,[1] DeLaire,[1] Baekeland,[1] and called "phenol resin" by Aylsworth.[1] But even after polymerization or hardening has been carried as far as possible, it is considerably less hard, less strong and less resistant to physical and chemical agents than the polymerization products resulting from the reaction of phenol on a sufficiently larger proportion of formaldehyde or equivalent substances.



In order to obtain the latter polymerization products of maximum strength, hardness, and maximum resistivity, an adequately larger amount of methylen group must be introduced before or during the act of polymerization. The introduction of this methylen group may be accomplished by at least three distinct methods:

First: Reacting directly with a sufficient amount of formaldehyde (or its equivalents) upon phenol.

[1] *Loc. cit.*

Second: Reacting with formaldehyde (or its equivalent) on phenol alcohol.

Third: Producing a fusible dehydration product of phenol alcohols or saliretin products, then reacting thereon with formaldehyde or its equivalents.

The preceding diagram describes very well all these relations:

FIRST OR DIRECT METHOD.

Direct Action of Phenol on Formaldehyde.—Phenol can be made to react on formaldehyde or its equivalents at sufficiently high temperature to produce directly an infusible, insoluble polymerization product of maximum strength and hardness (Bakelite C). In this reaction, the main requirement is that a sufficient amount of formaldehyde or its equivalents *should enter into reaction*. For this purpose, it is not necessary nor sufficient that the required amount of formaldehyde be merely present; because some of the formaldehyde may not enter into reaction or be lost during the operation. *The principal requirement is that the formaldehyde should react in sufficient amount on at least a portion of the phenol present*, even if some of the latter remains uncombined in the mass.

By the use of suitable methods, this reaction can be interrupted at its initial stages so as to produce initial or partial condensation products which are temporarily fusible and soluble before further application of heat has changed them. These initial condensation products may be liquid, or pasty, or under specially favorable conditions, for instance by the use of small amounts of some bases, they may be prepared in solid form. At any rate, they are soluble in alcohol and acetone, and the solid variety is fusible. These fusible soluble initial products should not be confounded with the further advanced and intermediate product B, as described in my paper on "The Synthesis, Constitution and Uses of Bakelite,"[1] because the latter is insoluble and infusible, although it has not acquired the maximum hardness and resistivity which further application of heat will bring forth by changing it to condition C.

Further action of heat upon these fusible and soluble initial condensation products will ultimately cause polymerization and produce the final infusible and insoluble product of maximum hardness, maximum strength, and maximum chemical resistivity (Bakelite C).

By heating mixtures of phenol and formaldehyde in suitable proportions at sufficiently high temperatures for a sufficiently long time, chemical condensation may take place without the addition of condensing agents or catalytic agents; however, under such unfavorable condition, the action is too slow and too difficult to control for technical purposes.

By the addition of acids or acid salts, the reaction may be hastened to the point of becoming violent. But the presence of acid bodies tends to develop disturbing side-products which lessen the technical value of the final product. Furthermore, in presence of an acid-reacting mixture, whenever there is a sufficient excess of phenol, we do not obtain the infusible, final product, but resins of the fusible saliretin or "shellac substitute" type. Things go quite differently if small amounts of bases are present during the reaction.[1] Small quantities of bases prevent radically the formation of fusible soluble saliretin products (shellac substitutes, Novolak, phenol-resin, etc.) and insure the formation of infusible, insoluble final products, even in presence of a decided excess of phenol. If the phenol be used in excess, it will be found in the final product as a solid solution. In fact, the excess of phenol may be exaggerated to the point that the final product becomes very flexible or assumes a gelatinous appearance, and swells considerably in certain solvents, like phenol, or alcohol, or acetone, without, however, entering into complete solution. In any case, this free-phenol-containing substance is infusible; in other words, the application of heat can no longer liquefy it, although higher temperatures may char or destroy it.

This behavior of the bases constitutes a radical difference from that of acids or other acid-reacting bodies. Whenever acid-reacting bodies are used in conjunction with an excess of phenol, or an insufficient amount of reacting formaldehyde, which amounts to the same thing, they tend to produce fusible soluble resins, while under exactly the same conditions and with the same proportions of phenol and formaldehyde, small amounts of bases develop *surely* infusible polymerized bodies as ultimate products.

In this method, the bases should be used in relatively moderate amounts; not in molecular proportions, as Manasse and Lederer[2] utilize them for making phenol alcohols, nor as DeLaire[2] employs them to produce the fusible resinous dehydration products of these phenol alcohols. Neither should they be used in such large quantities nor under such conditions as Hentschke[3] recommended for the manufacture of certain antiseptic compounds.

If the amount of base be properly restricted, the reaction proceeds very regularly and remains under easy control. The base acts as an excellent accelerator, both in the condensation and in the polymerization. The use of bases under the above mentioned conditions enables one to carry out the reaction with the utmost uniformity and certainty of results.

At first sight the importance of these seemingly modest facts is not very apparent; no more than the value of the observation that sufficient counterpressure permits quick polymerization at high temperatures without risk of porosity; no more indeed than the realization of the fact that the final product with its great hardness, its strength and other splendid qualities is unelastic and wofully deficient for most industrial purposes where great resistance to shock or vibration is required, and that the incorporation of suitable fibrous materials improves all this by modifying the shattering wave induced by impact. Yet these three main factors have enabled us to harness into technical service an elusive laboratory reaction and have rendered possible the creation of a new industry which is gaining daily in importance.

[1] THIS JOURNAL, **1**, No. 3, 149 (1909).

[1] See Baekeland, U. S. Patent 942,809.

[2] *Loc. cit.*

[3] Hentschke, D. R. Patent 157,553.

It has been shown[1] that small amounts of ammonia or amines may be used to good advantage for this purpose. It is a well known fact[2] that ammonia or ammonium salts in presence of formaldehyde produce instantly a corresponding amount of hexamethylentetramin. In the same way, if any ammonia be added to a mixture of phenol and formaldehyde, a corresponding amount of hexamethylentetramin is produced which can easily be extracted from the mixture. This fact was confirmed by Lebach, and can easily be ascertained by direct experiment.[3] It is self-evident that instead of a mixture of phenol and formaldehyde and ammonia, an equivalent amount of hexamethylentetramin or hexamethylentetramin-triphenol[4] may be used.

So that in the preparation of these bodies, formaldehyde can be replaced by hexamethylentetramin; this was already published by Lebach in the patent literature as far back as the end of 1907.[5] Whether the phenol mixture be prepared with ammonia or with hexamethylentetramin, its properties are practically the same, and on heating, both mixtures engender the same product, with the final evolution of ammonia gas.

Whatever be the methods employed, this reaction is strongly exothermic, and heat is set free in the two phases of the reaction: *First*, in the condensation stage, by which the initial product is formed, and water is separated. *Second*, in the final hardening when the product becomes infusible by polymerization, a considerable disengagement of heat takes place anew. If the substance be heated in thin layers, this self-heating may be unobservable on account of the heat losses; under such conditions, if, however, the mass is thicker or bulkier, and more especially if it be contained in a mold, this self-heating becomes very disturbing and liberates gaseous or volatile products which cannot escape before the mass sets to infusibility; this causes the mass to swell and raise and to become porous, and makes it practically worthless for almost all technical purposes. This was the stumbling block which former investigators tried to avoid by conducting the hardening at very low temperatures, or by the use of suitable solvents which tend to moderate the reaction. This tendency towards foaming exists also if acid-condensing agents are used, or even if no catalytic agents are added at all. The liberated gaseous products may vary according to conditions; in some cases, they may consist largely of formaldehyde gas which tends to escape before the reaction is accomplished; if ammonia be used, and more so if hexamethylentetramin be employed, varying amounts of ammonia gas will be set free.

Especially when hexamethylentetramin is used, the evolution of ammonia is very abundant, and this naturally increases the tendency to foam and to give a porous final product. This tendency to foam becomes pronounced only at temperatures above 50° or 100° C., because at these increasing temperatures the exothermic reaction sets in. It should be noted that temperatures considerably higher than 100° C. are those which are employed in almost all commercial applications of these products, because they allow quick hardening and quick molding. At such high temperatures, polymerization proceeds very rapidly, but the exothermic reaction superinduces a further spontaneous increase of the temperature of the mass, and in this way, the defect of foaming is considerably more pronounced.

This tendency to foam makes it of the utmost technical importance whenever high temperatures are employed, for quick commercial work, that the liberation of gaseous or volatile products during the polymerization or hardening process, should be opposed by a suitable counter-pressure. The latter may be applied in various ways; for instance, by heating in closed molds or in closed vessels, so that the imprisoned gases develop a suitable counter-pressure; or by heating in a chamber in which air or other gases have first been pumped to a suitable pressure; or by heating in a hydraulic press. In the latter case, the first function of the pressure is to counteract the development of gaseous products, while at the same time the mass is given the desired shape in the mold.[1]

For other applications, like varnishes or lacquer, where the material is applied in thin layers, the use of counter-pressure is not indispensable.

As stated above, the use of ammonia or hexamethylentetramin increases the tendency to foam. On the other hand, small amounts of fixed alkalies, like caustic soda, act as more powerful accelerators than ammonia or hexamethylentetramin, without causing the evolution of disturbing ammonia gas or other gases. In this and other respects, the fixed alkalies have decided advantages over ammonia or hexamethylentetramin, as well as over acid-condensing agents. For instance, they permit rapid hardening at the relatively low temperatures of 70° to 95° C.; furthermore, as soon as the initial solidification has set in, the temperature can be raised quickly to 110°, 120° and 160° C. At these higher temperatures, the hardening proceeds with great intensity and without fear that the gas bubbles should cause porosity. If the heating be carried to the hardening temperature before all the water has been first expelled, then the only necessary precaution will be to keep the temperature sufficiently below 100° C. so that there can be no evolution of steam which might cause blisters; but as soon as the mass has been heated long enough at these lower temperatures, so that it has solidified sufficiently, the temperature can be raised with impunity above the boiling point of water. As soon as these higher temperatures become available, the polymerization to final hardening advances very rapidly.

For many purposes, it is simpler to drive off the water at temperatures below the polymerization temperature, either by drying *in vacuo*, or by drying in a

[1] Baekeland, U. S. Patent 942,809.

[2] Wohl, *Ber.*, **19,** 1892; Tollens, *Ibid.*, **17,** 653; Carl Goldschmidt, page 29, Bonn, Verlag von Friedrich Cohn, 1903; Cambier, Borchet, *Compt. rend.*, **120,** 557.

[3] Lebach, *Zeit. angew. chem.*, **1909,** 1600.

[4] "The Addition Product of Phenol and Hexamethylenetetramin," see Beilstein, *Handb. der Organ. Chem.*, (3) **2,** 651

[5] Knoll, Belgian Patent, *loc. cit.*, and Wetter (Knoll), British patent, *loc. cit.*

[1] Baekeland, U. S. Patent 942,699.

stove at ordinary pressures at moderate temperatures, for instance 50° C. or below. Such dried material can now be submitted directly to relatively high temperatures without risk of blistering or foaming. This gives us the very best means for rapid hardening, as required by commercial processes. The use of these fixed alkalies has enabled us to carry on hardening and molding at a faster rate than is possible with ammonia or hexamethylentetramin, or other means, and at the same time to produce molded articles of better heat-resisting qualities, of highest resistivity to solvents, chemicals, and of excellent dielectric properties. For many electrical purposes, the fact that no free ammonia exists in the mass is a further advantage; indeed, this free ammonia is slowly liberated by heat from molded articles and sometimes may play rather disturbing pranks. It has a tendency to corrode brass articles.

SECOND METHOD.

Action of Formaldehyde or its Equivalents on Phenol Alcohols.—I have described this process in 1908.[1] It has been shown that the best results are obtained if the amount of formaldehyde is at least one-sixth of a molecule as calculated to one molecule of phenol alcohol. This same ratio holds good if substances equivalent to formaldehyde or to phenol alcohols are used.

This method has enabled us to gain clearer insight into the relations of all infusible condensation products to the phenol alcohols, and has furnished us the theoretical means for determining the optimum quantities of reacting materials in our technical methods of manufacturing. However, this process is more of theoretical than of practical interest, in as far as the third method accomplishes substantially the same result by starting from the anhydrides of phenol alcohols.

THIRD METHOD.

Action of Formaldehyde or its Equivalents (Paraform, Hexamethylentetramin, etc.) on Saliretin-Resins.—The method is another indirect method and consists in first preparing a saliretin-resin of the fusible soluble type, then reacting thereupon with formaldehyde or an equivalent of formaldehyde.[2] This method was first published by Lebach at the end of 1907.[3]

In these patents, it is clearly mentioned that paraform and hexamethylentetramin are equivalent to formaldehyde in the preparation of condensation products. Furthermore, it is described how the condensation products may be prepared in two successive steps by adding the formaldehyde or hexamethylentetramin, or other equivalents, in two successive quantities. Briefly stated, the process consists in first preparing a fusible saliretin-resin; to this resin is mixed a second quantity of formaldehyde, paraform, or hexamethylentetramin; this mixture submitted to heat produces the infusible product C. In reality, we prepare here in two steps a product which is practically similar to the solid initial condensation product described in the first or direct method. In that method the initial condensation product is obtained more directly by the addition of a sufficient amount of formaldehyde to phenol, in presence of ammonia, or other bases, or by the equivalent use of hexamethylentetramin or paraform. In the first or direct method, the reaction between the phenol and the formaldehyde ensues under elimination of water due to so-called chemical condensation. In the present case, however, a portion of the formaldehyde is first made to react on an excess of phenol, bringing about a corresponding elimination of water by chemical condensation; but in as far as the amount of formaldehyde is insufficient, fusible saliretin-resin is formed. In order to transform the latter into the product C, it is necessary to supply an additional amount of formaldehyde, or some paraform, or hexamethylentetramin, etc.; hence the necessity of adding a certain amount of those methylen compounds to the fusible saliretin-resin, before the mass is submitted to hardening or polymerization by heat. The chemical reaction of the methylen compound on the fusible saliretin-resin is accompanied by the further elimination of water which can easily be demonstrated by direct experiments.

If hexamethylentetramin is used, an abundant liberation of ammonia takes place at the same time; but even with the use of the latter, a certain amount of water is liberated by the action of the hexamethylentetramin on the free phenol contained in the fusible soluble saliretin-resin.

Barring those minor differences in preparation and proportions, the final product C is practically the same as that obtained by the first or direct method as described above.

If hexamethylentetramin be added to the fusible resin, and heat be applied, the violent exothermic reaction which ensues causes an abundant liberation of ammonia gas. The mass raises like bread, and a hard spongy product is the result. Aylsworth[1] utilizes this foaming to prepare this substance in powder form by first producing porous masses of the final condensation product which can be crushed more easily to a fine powder than if solid lumps of this refractory material have to be pulverized.

In molding processes where high temperatures are needed, so as to insure hardening, this violent liberation of ammonia gas can easily be counteracted by suitable counter-pressure. In this case, the pressure is not only required for shaping the article, but first and foremost, for avoiding porosity. This can easily be demonstrated by heating the mass in an open mold, at the same high temperature as is used in the press; under these conditions, direct application of these high temperatures causes foaming and porosity unless suitable counter-pressure be applied.

It has been claimed that by the use of hexamethylen-

[1] "The Synthesis, Constitution, and Uses of Bakelite," *loc. cit.* See also Baekeland Belgian additional patent 213,657; Baekeland French additional patent 11,628.

[2] Baekeland, U. S. Patent 1,038,475.

[3] Knoll Belgian patent 204,811, Dec. 31, 1907, and Wetter (Knoll), British patent 28,009, 1907, all owned by the Bakelite Gesellschaft, of Berlin.

[1] Aylsworth, Belgian Patent 240,116.

tetramin in connection with perfectly dry fusible soluble phenol-resin, no water is liberated, which is supposed to be an advantage for certain applications where high dielectric properties are required. However, it should be noted that such fusible soluble phenol-resins all contain considerable amounts of free phenol and by the action of hexamethylentetramin on this phenol, water is formed besides the ammonia that is set free.

Moreover, the presence of large quantities of free ammonia is, if anything, more objectionable for certain purposes than the possible presence of small amounts of water.

It is true that free ammonia can be expelled by sufficiently long after-drying of the molded articles, but by the same means it is just as easy to expel the last traces of water. The most striking fact is that there is no serious difficulty in obtaining articles of extremely high dielectric properties, even when starting from raw materials containing considerable amounts of water, provided the manufactured articles be submitted afterwards to a drying treatment which can be performed in any suitable drying stove.

It should be noted that almost all molded commercial articles made of phenol-formaldehyde condensation products contain various amounts of fibrous materials, preferably wood pulp or finely divided sawdust. These organic fibrous materials, at the high temperature at which the molding in the hydraulic press takes place (140° to 160° C., or over), begin to liberate variable amounts of water and other products of decomposition, which depress the dielectric properties. This is another reason why all molded articles intended for purposes where high dielectric properties are essential should be submitted to oven-drying after they are molded. Those who are unfamiliar with the technical side of the subject may ask why it would not be simpler to omit altogether the use of fibrous organic materials. They might suggest the use of asbestos. But asbestos has other drawbacks, which limit its use. For instance, asbestos is a relatively poor insulator, and the strength imparted by its fibers is not so great as that imparted by vegetable fiber; furthermore, its specific gravity makes the articles compounded therewith very heavy; moreover, any asbestos compositions which have to be machined or milled are very severe on the tools. Another objection is that asbestos compositions do not take the excellent and easy polish which can be so easily developed on articles made with wood-fiber compositions, nor do they possess the elasticity and strength of the latter.

It might also be suggested to drop entirely the use of any fibrous material, and to use amorphous or pulverulent fillers. But the technical requirements forbid this. Indeed, the main characteristic of the final phenol-formaldehyde condensation products, is that although they are exceedingly hard and resistant and have a remarkably high crushing strength, their flexibility and elasticity are very limited. In regard to these latter qualities, they occupy a position between hard rubber and glass. A sudden shock or limited bending shatters them, and this would restrict enormously their technical applications. I found that the shattering wave induced by impact could be considerably modified by the suitable introduction of fibrous or cellular materials, like wood-fiber. This behavior is quite different from that of other plastics like celluloid or rubber, which lose their best and characteristic qualities by the incorporation of filling materials. The phenol-condensation products, on the contrary, are enormously improved for commercial use, if compounded with filling materials, provided the latter be of a fibrous nature; in the latter case, they lose their natural brittleness and can stand shock and impact, without shattering; they can be rendered flexible and yet maintain all their other excellent properties of high resistivity to physical and chemical agents.

Hence, some of the most important industrial applications of these condensation products are precisely those where they are used in conjunction with fibrous bodies; for instance, they serve to impregnate fibrous materials like wood, pulp-board, and to indurate the latter, or to agglutinate firmly loose fibrous substances, like wood-fiber, or fine sawdust, which then act as a structural skeleton distributed throughout the indurated mass.

This important technical result is easily demonstrated by comparing the enormous strength and resistance to impact or shock of molding compositions containing wood-fiber with others containing the same amount of structureless filling materials, for example, powdered materials. Compositions made with the latter will be found incomparably more brittle and very much less appropriate, if not entirely unsuitable, for most industrial purposes, more especially for molded articles where great strength is required.

Other important technical results are accomplished with the use of filling materials; for instance, the highest dielectric properties have been rendered possible by the joint favorable action of fibrous material and heat and pressure.

It might be cited here that paper impregnated with these condensation products, and submitted to hardening under heat and pressure, has made it possible to manufacture sheets which show an astonishingly high disruptive test (puncture test), averaging 77,000 volts a. c. on sheets of $^1/_{18}$ of an inch thickness corresponding to 1,230 volts per mil. or about 48,500 volts per millimeter.

Under these favorable conditions, the vegetable fiber of the paper is thoroughly impregnated with the condensation product, and the high pressure has excluded the possibility of porosity induced by foaming.

YONKERS, N. Y.

LABORATORY AND PLANT

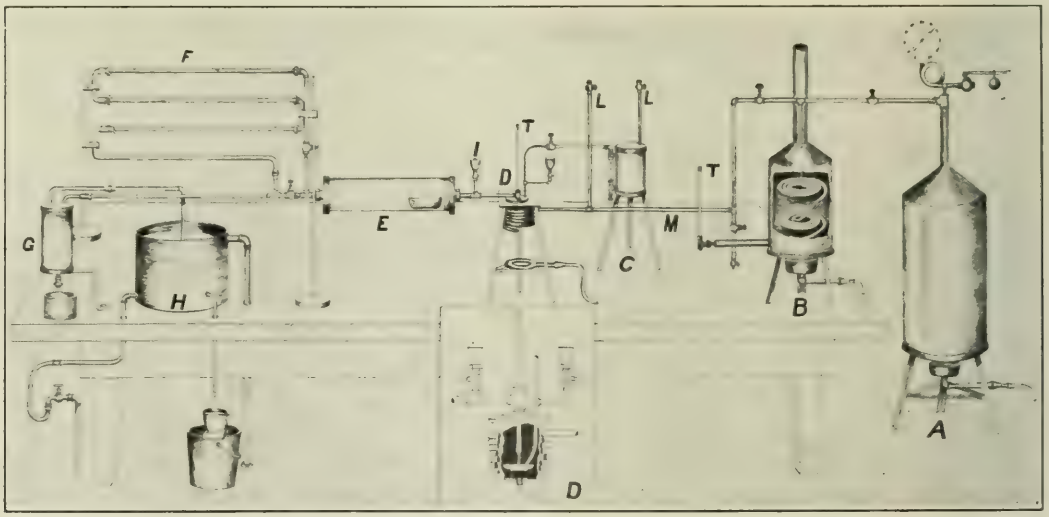
APPARATUS FOR THE EXAMINATION AND STUDY OF THE BEHAVIOR OF VALVE AND CYLINDER OILS AND OTHER PETROLEUM LUBRICATING OILS IN SATURATED AND SUPERHEATED STEAM, CARBON DIOXIDE, AIR AND OTHER GASES.[1]

By P. H. Conradson [2]

The introduction of a high degree of superheated steam in locomotive and stationary engine practice has brought about the necessity of adding tests to the ones usually made of cylinder oils, whether straight petroleum stock, or mixture of the same with smaller or larger amounts of saponifiable fats.

The writer has constructed and used an apparatus for some time in the investigation of cylinder oils suitable for the lubrication of valves and cylinders in connection with the use of highly superheated steam in locomotive service.

The apparatus is essentially as follows (see photographic cut):



A, small steam boiler with gas, steam gauges and pipe conditions.

B, superheater with armored thermometer, T, and steam connections (a small circulating water heater with double copper coils, answers very well).

C, sight feed lubricator with connections.

D, steam vessel (a conical cast iron retort for distilling mercury, about 95 mm. deep and about 75 mm. in diameter at top provided with two strong screw clamps to keep the lid tight, answers very well) surrounded on the outside, as indicated, by a coil of copper pipe 5–6 mm. inside diameter, for further heating of the steam and gases used in the tests: this coil is tapped into the bottom of the steam vessel containing a suitably supported dish of about 25 cc. capacity (an ointment box about 55 mm. in diameter, 18–20 mm. high) into which the oil to be examined is fed drop by drop from the sight feed lubricator C (or a given amount of oil is poured into the cup I). Through the lid is inserted an armored thermometer, T, reaching down into the dish. The steam vessel thus arranged and connected is surrounded and covered by a suitable asbsetos hood.

L, pipe connections for the gases used.

E, heavy glass cylinder about 200 mm. long and 18–20 mm. inside diameter containing a small rectangular boat or dish; beyond E is a glass tubing system, F, connected up as shown with brass fittings; each glass tube is about 500 mm. long and 8–9 mm. inside diameter; at the further end is attached a steam separator and oil collecting vessel, G, consisting of an ordinary glass chimney fitted up with brass caps; to this condenser H is connected by means of copper tubing

In this apparatus any desired temperature may be maintained at least up to 1000° F.; this is 300°–400° higher than is required under the most exacting service conditions as far as superheated steam temperature is concerned.

In studying the behavior of valve and cylinder oils in an atmosphere of superheated steam, the steam is passed from the small steam boiler through the superheater B and into the steam vessel D through its pipe coil (lamp being lit under D), and out through E, F, G and H.

When the temperature reaches and is regulated in D to 400° F., oil is fed drop by drop from sight feed lubricator C (or the cup I is filled); the steam is shut off and the valve in C (or I) opened, letting the oil run into the dish in D; the steam valve is then very gradually and carefully opened so as to let through any desired amount of steam.

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

[2] Chief Chemist, Galena-Signal Oil Co.

The temperature in D is maintained for a given length of time at or near 400° F., noting if any oil vapors are coming over; by shutting and opening the steam valve it is easy to see if any vapors are coming over with the steam.

The temperature is increased in increments of 25°–50° F., at a time, until the desired temperature is reached, noting the behavior of the oil vapors passing on with the steam through the glass pipe system, etc. It is interesting to note that cylinder oils containing rather a large percentage of saponifiable fats or fat oils generally come over at much lower temperatures than the main portions of the petroleum stock oils that are commonly used in compounding first class cylinder oils.

In further study of the behavior of oils, the boat in the glass cylinder E may be filled through the cup I to the left, and subjected at various temperatures to slow currents of superheated steam, carbon dioxide and air or mixtures of the same. The glass cylinder E during the last test is surrounded by a heavy asbestos covering to prevent radiation.

The cylinder oils may leave a residue in the dish in D at steam temperatures below 700° F.; if so, such residue should give a clear solution in 90 cc. of 0.65 sp. gr. (87° B.) petroleum ether (Pennsylvania) and show no precipitate on standing. At steam temperatures of 850°–900° F., all the oil has usually volatilized with the steam; good oils should leave no carbonaceous or coky residue.

While this apparatus was designed principally for the study and behavior of valve and cylinder oils in atmospheres of steam at various temperatures, it can be adapted very readily for the study of other oils at various temperatures in currents of air, carbon dioxide or other gases or mixtures of same with and without steam.

The accompanying table of comparative tests of five samples of cylinder oils, A, B, C, D, E and F, a petroleum distillate of interest in connection with the study of cylinder oils in superheated steam:

	A.	B.	C.	D.	E.	F.
Flash point (open cup)	545° F.	550° F.	605° F.	595° F.	550° F.	365°F.
Burning point	610° F.	630° F.	695° F.	680° F.	630° F.	415°F.
Gravity at 60° F. Baumé	26.4	26.1	24.7	25.9	..	33.5
Sp. gr. at 15° C.	0.895	0.897	0.905	0.898	...	0.856
Color	Light	Dark	Dark	Very dark		Yellow
Gas, test before fire test	Good	Good	0.5 cc.	4.0 cc.	..	...
Gas, test after fire test	Good	Good	Good	3.0 cc.	...	...
Cold test flows	+55° F.	+32° F.	+45° F.	+34° F.	+30° F.	Zero
Saponifiable fats	Trace	Trace	Trace	Trace	15 per cent.	None
Vis. Saybolt at 212° F. (60 cc.)	133 sec.	146 sec.	215 sec.	216 sec.	.	.
Barbey Ixomet 500° F. (180 units = 30 cc.)	45 sec.	51 sec.	61 sec.	60 sec.	..	..
Hot air test at 540° F. (loss)	15 per cent.	11 per cent.	2.5 per cent.	5.5 per cent.	...	.
Gas, test after	Good	Good	0.5 cc.	3.5 cc.	..	.
Carbon test residue	2.15 per cent.	2.70 per cent.	4.90 per cent.	5.10 per cent.	...	...
SO_2 in residue	0.023 per cent.	0.03 per cent.	0.03 per cent.	0.04 per cent.	...	...
Loss in superheated steam at 400° F.	0.0 per cent.	0.0 per cent.	0.0 per cent.	0.0 per cent.	0.0 per cent.	32 per cent.
Loss in superheated steam at 500° F.	5.0 per cent.	4.0 per cent.	1.5 per cent.	1.0 per cent.	5.0 per cent.	67.0 per cent.
Loss in superheated steam at 600° F.	18.5 per cent.	18.0 per cent.	6.5 per cent.	8.5 per cent.	21.5 per cent.	...
Loss in superheated steam at 700° F.	44.0 per cent.	34.0 per cent.	32.5 per cent.	40.5 per cent.	...	...
Total loss up to 700° F.	67.5 per cent.	56.5 per cent.	40.5 per cent.	50.0 per cent.	26.5 per cent.	99.0 per cent.
Gas test of oil: Residue from 700° test	Good	Good	1.5 cc.	3.0 cc.	..	...

Hot Air Test = 13 grams oil in shallow round flat bottom iron dishes exposed six hours at 540° F. in a specially designed air bath.

Gasoline Test = 10 cc. oil, 90 cc. petroleum ether 0.65 sp. gr. (from Pennsylvania crude) in graduated flat precipitating tubes, taking reading after 1 hour's standing.

Carbon Test using 35 grams Oil, according to Conradson's apparatus and method.

Superheated Steam Test = 13 grams of oil used.

Sample "A" in a superheated steam test at 800° F. (427° C.) left no residue. Sample "C" left 2.5 per cent. dry carbonaceous residue.

Sample "E" containing 15 per cent. of saponifiable fats subjected to the superheated steam test lost 26.5 per cent. up to 600° F.; the oil residue from this test contained 17.5 per cent. saponifiable fats; this indicates that the petroleum oil stock ("B" used) goes off with the steam somewhat faster in proportion to the fat oil up to 600° F. (350° C.).

The steam pressures used in these tests were about ten to twelve pounds per sq. in. A large volume of superheated steam passed through the apparatus during the tests (about 40 cc. condensed steam per minute).

In these superheated steam evaporating tests about 13 grams of oil were weighed into the small dish placed inside the steam vessel D. (The capacity of the small iron dish is 50 cc. having a diameter of about 48 mm. and 30 mm. high, with flat bottom.)

The steam vessel with the oil in the dish was heated up to about 350° F. (176° C.), passing a slow current of natural gas through the apparatus, then superheated steam was admitted, the gas shut off, and the temperature raised up to the required degree and kept constant for about 75 minutes; the volatile matter in the oils at the given test temperature generally were carried over with the steam inside of 60 minutes, allowing about 15 minutes' extra steaming. At the end of each given temperature test the steam and heat were shut off; after cooling, the dish containing the oil was weighed and replaced in the steam vessel and the operation repeated for the next temperature test.

GALENA-SIGNAL OIL COMPANY,
FRANKLIN, PA.

A NEW CALORIMETER BOMB WITH SPECIAL ADVANTAGES AS TO MATERIAL OF CONSTRUCTION AND METHOD OF OPERATION.[1]

By S. W. Parr

In attempting to improve upon the oxygen bomb for calorimetric use, the efforts have been directed along two distinct lines to meet what seemed to be the most pressing needs of the case: *first*, the discovery of some substitute for platinum which would resist the corrosive action of the acids formed and, *second*, the improvement of the methods for closing the receptacle so that a perfect seal could be secured with certainty and ease.

With reference to the first item, the development of a substitute for platinum, the problem is not without serious difficulties. It is to be borne in mind that in many instances, as with coals and similarly constituted substances, the nitric acid resulting from the combustion is produced under the best possible conditions for promoting a solvent action. The concentration of the acid in the bomb after a reaction is considerable. Moreover, the temperature, at least for a short period, is relatively high and the presence of corroding gases under high pressure may contribute to the activity. Again, in many substances a high percentage of sulphur exists and this burns to SO_3 or in the atmosphere of the interior, saturated as it is with water vapor, to H_2SO_4. For example, a very large part of the coals of the Mississippi valley have a content of sulphur amounting to 3 or 4 per cent. of the gross weight of the coal. Indeed, a content of sulphur is not infrequently met with of five and even six per cent. We have then in these cases of common occurrence conditions wherein both sulphuric and nitric acids are formed and these of a rather concentrated character. One of the common methods of counteracting the action of the acids is by use of some sort of resistant covering. As will be seen later, the method devised for closing the bomb involves the machining of the parts of dimensions accurate within $^1/_{50}$ of a millimeter. This feature, therefore, would make it impracticable to make use of an enamel as a protective covering. This expedient is also found, in practice, to be objectionable, owing to the frequent ruptures that are certain to occur in the enameled surface, thereby admitting the acid to the metal beneath. So far as a platinum lining is concerned in the device contemplated, and this was given an extended trial, the difficulties were as follows: First, the cost of platinum, representing at the current prices approximately $400 per bomb, made the use of that metal prohibitive, especially where a considerable number of bombs were desired such as for use with large classes. Second, the method of closing the bomb called for an exact relationship as to dimensions, and, as in the case of enameling, this could not easily be secured or maintained with an inner shell or lining. Moreover, the device to be employed for the inlet valve was such as to make it a very difficult problem of construction to make use of a second metal in that part of the apparatus. Third, the inevitable corrosion which sooner or later begins under the platinum shell roughens the surfaces, especially those coming in contact with the gasket. In time the entire surface under the platinum is affected and the water equivalent as well as the strength of the bomb is modified. These reasons alone, even if there were no others, are quite sufficient for indicating that the bomb, if made at all in conformity with the design contemplated, should be made of a metal capable of being machined to exact dimensions and in conformity with a desired pattern.

For this purpose, therefore, a study of alloys was undertaken with a view to determining if one could be devised sufficiently resistant to acid to effectually replace platinum, and that at the cost in the massive form necessary to easily compete with that metal. It must be possible, moreover, to either cast or stamp the metal into proper form suitable for machining into the final and exact shapes desired. The alloy finally developed has proved to be eminently satisfactory as far as its acid-resisting properties and strength are concerned. It is complex in composition, having as the chief components nickel, copper, tungsten and chromium with smaller and more or less adventitious amounts of manganese, aluminum, titanium, boron and silicon. The details of composition and properties of the alloy as finally adopted are presented under another title.[1] Concerning the securing of this material in forms suitable for machining to the desired patterns, only the method of melting and casting has so far been undertaken. The difficulty of securing perfect castings has seemed at times almost insurmountable. This is due to the fact that the melting point of the alloy is relatively high, approximately 1300°, and at the point of solidification the shrinkage is so great that cracks or flaws are opened up which render the casting unfit for use. Again, the occlusion of gases at the high melting temperature is great and pin holes are apt to be a source of much annoyance. The overcoming of these difficulties is, however, a mechanical rather than a chemical problem and need not be entered into here.

That the material may fairly be considered a substitute for platinum in the service here described is shown in the article above referred to, wherein is given a table of solubility tests. Also in another article accompanying this discussion[2] data are given upon a bomb of this new material in practical operation, which indicate that the alloy is entirely suited for use in the manner described.

The second improvement sought for relates to the method of closing the receptacle. The difficulties attending the use of lead gaskets relate chiefly to the stress and strain required to secure a perfect seal. Other objections relate to the chemical action upon the lead, and to the pitting or corrosion of the needle valve or seat, making it necessary to frequently reseat or repoint the valve parts. The substitution of rub-

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

[1] "A New Alloy with Acid-Resisting Properties," by S. W. Parr, Inorganic Section (Sec. II) this Congress.

[2] "Some Tests on a New Calorimeter Bomb," by Richard H. Jesse, Jr., This Journal, p. 748.

ber for lead is found to be entirely practicable if the conditions under which it is used are such that flame or any of the processes of combustion are not allowed to come in contact with the rubber. This is easily accomplished by interposing between the rubber gasket and the inner chamber a shoulder of massive metal so constructed that the cross section of the space between the two metallic parts is so small, say $^1/_{25}$ of a millimeter, and the longitudinal measurement of the space, that is the distance from the rubber to the inner chamber, is so great, say $1^1/_2$ or 2 millimeters, that the combustion processes may not travel along so narrow a passage and therefore do not come in contact with the rubber gasket. This principle is carried out in closing the main opening of the bomb and also in closing the valve through which oxygen is admitted. This will be made clear by reference to a sketch.

In Fig. 1, *B B* are the walls of the bomb which enclose the space *O*. The cover *C* is made with an encircling rim, *R*, which retains the rubber gasket *G*. The cover is so made that a shoulder, *S S*, passes the wall of the bomb as it comes up to position against the gasket. The machining of the parts is such that the space between the shoulder and the wall is about $^1/_{25}$ mm. Moreover, the distance from the lower edge of the shoulder to the gasket is about 2 mm. This is increased slightly by the pressure of the cover upon the gasket when the screw cap is brought down upon it. Conditions are thus secured which prevent the traveling of flame or any of the processes of combustion from the combustion chamber *O* to the rubber gasket *G*. The same principle is observed in the arrangements for the inlet valve *V*. The small gasket *g* is protected from the reactions or heat of the combustion chamber by narrow passages between metal walls.

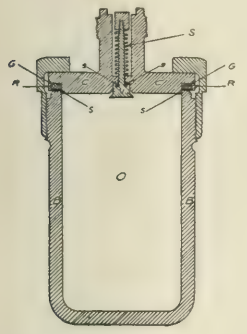


Fig. 1.

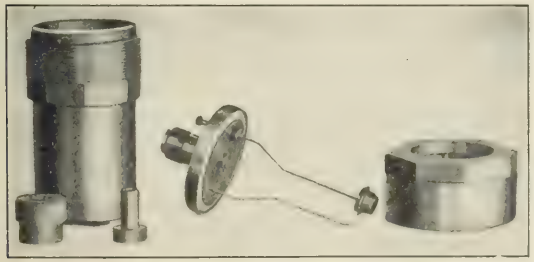


Fig. 2.

In this manner it is entirely possible to secure a perfect seal with a minimum amount of compression, by use of rubber gaskets and this without any burning whatever of the rubber.

A word further as to convenience of operation. The valve *V* works automatically thus: The valve is held lightly in place by the springs, but upon the admission of the oxygen above the valve it is forced downward admitting the gas to the chamber *O*. When the proper amount is admitted, say 25 atmospheres, the oxygen supply is shut off and immediately the valve is lifted into place by the spring. The strong pressure from within tends to seat the valve more firmly in place. After an extended experience with this type of valve, involving numerous modifications, the present form shown herewith has been found to be exceedingly effective and satisfactory. Thumb pressure on the top of the stem is found sufficient for releasing the gas at the close of an experiment. The most striking characteristic, however, in the manipulation of the bomb is the ease with which the cover may be fastened to withstand the necessary pressure without leakage. As may be seen in the accompanying illustrations, a simple octagon plate is set into the table or shelf and an octagon wrench about 50 cm. long affords ample leverage for screwing down the cap and seating the cover. The expenditure of a great amount of force in this part of the procedure is quite eliminated. The ease and readiness with which a perfect seal can thus be obtained have done much to revolutionize the work of operating a calorimeter of the oxygen bomb type.

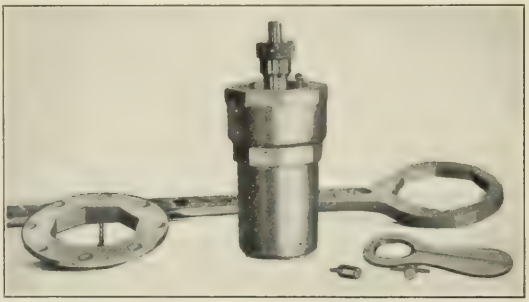


Fig. 3.

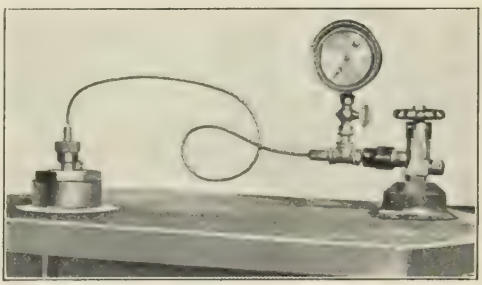


Fig. 4.

Fig. 2 shows the cover and screw cap removed from the bomb. The small parts at the base of the bomb are couplings for oxygen connection at the top of the cover.

Fig. 3 shows the bomb with the parts assembled

with the octagon holder and wrench for setting the screw cap.

Fig. 4 shows the shelf fittings and connection with the oxygen tank. The shelf is hinged at the left-hand edge. It may be unfastened at the right-hand edge and lifted for the removal of the tank when it is required to renew the supply of oxygen.

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SOME TESTS ON A NEW CALORIMETER BOMB.[1]

By RICHARD H. JESSE, JR.

In connection with the preceding description of the new alloy bomb of nickel-copper-chromium[2] it may be of interest to report briefly the results of a series of experiments on the combustion of two standard substances, cane sugar and benzoic acid. These experiments were undertaken not only for the purpose of standardization but also to test the behavior of the instrument under actual working conditions.

The principal features of difference between this bomb and other types are: (1) the substitution of an alloy, very resistant to the action of acids, for the usual platinum, gold, or enamel lining; (2) the use of a well protected rubber gasket for sealing the bomb instead of a gasket of lead; (3) the replacement of the ordinary steel needle-valve by a seated valve bearing a rubber gasket. For one who has spent much physical and mental effort in trying to seal completely bombs fitted with needle valves and gaskets of lead and gold, a very short experience is sufficient proof of the superiority of the present method of sealing in so far as speed and ease of manipulation are concerned. Former experience in this laboratory has offered evidence that these features do not cause a decrease in the accuracy desired for commercial fuel analysis. It has remained, however, to prove that they will answer the purposes of investigations where the highest attainable accuracy is desired.

A series of semi-quantitative corrosion tests in which specimens of the alloy were exposed at ordinary temperatures and for varying lengths of time to the action of 4 *N* sulphuric and nitric acids and mixtures of the two have indicated that the amounts of alloy which would dissolve in the time of a determination are negligible. To test the corrosion under working conditions, the washings from eight runs, which had been titrated in the usual manner for nitric acid with potassium hydroxide, were combined and analyzed for copper and nickel. The copper was precipitated by hydrogen sulphide in acid solution and was weighed as cuprous sulphide; the nickel was determined by the dimethylglyoxime method. In the eight determinations 1.6 milligrams of copper and 6.2 milligrams of nickel were dissolved. In a single determination therefore we have the solution of 0.2 mg. Cu and 0.8 mg. Ni. The quantity of the metal nitrates would have a heat of formation of approximately 1.8 calories.[1]

Since in these experiments the total amount of heat measured in a run was 9500 calories, about 0.02 per cent. of the rise was due to the solution of the alloy. This is a quantity which cannot be directed with certainty even in the very best calorimetric work. This particular bomb was the first successful casting. Since the work was begun, there have been slight modifications in the composition of the alloy which have probably increased its acid resistance. Quantitative evidence on this point is, however, lacking as yet. In coal calorimetry, sulphuric acid will be present in addition to the nitric acid. The corrosion tests already mentioned show that the mixture of these two acids is not much more active than nitric acid alone.

There is only indirect proof to show that the use of rubber gaskets is without effect on the accuracy of the bomb. The construction of the instrument is such that the rubber is well protected. The portion of the gasket which comes in contact with the gases in the bomb is a ring about $^{1}/_{1000}$ inch in width; to reach this the hot gases have to pass through a very narrow space with massive metal on each side so that they would almost certainly be cooled below the danger point. In these experiments there was absolutely no smell of burnt rubber in the bomb after a combustion. The constancy of the results given below is further proof that the rubber has no harmful effect, because it is hardly conceivable that if the rubber were burnt at all it should be burnt in such constant amount each time.[2]

The method of adiabatic calorimetry[2] devised by T. W. Richards was used for these combustions.

The principle of the method is that the calorimeter is surrounded on all sides and on top by a bath of caustic soda, the temperature of which is at all times kept the same as that of the calorimeter. By running in sulphuric acid in measured amounts the temperature of the bath can be readily changed so that it conforms to that of the calorimeter even during the first rapid rise. This method has already proved itself capable of extreme accuracy. The mercury thermometer used was of the Beckmann type and was calibrated by the Bureau of Standards. The results with it were very satisfactory. Three different samples of sugar were used. They were supplied at different times during the past three years by the Bureau of Standards. Two samples of benzoic acid were burnt, one from the Bureau of Standards and one that had been carefully purified in this laboratory; experiment marked No. 10 was on the latter sample. The agreement is all that could be desired.

All the experiments fell within the temperature range 21–25° C. Since the temperature rise measured was about 3°, it follows that the mean temperature of any experiment did not differ from that of any other

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

[2] This bomb was devised by Professor S. W. Parr, of this laboratory, and is described in the preceding paper.

[1] Thomsen's results in Landolt-Börnstein:

$Ni + 2N + 6O + Aq = Ni(NO_3)_2Aq + 113{,}200$ cal.

$Cu + 2N + 6O + 6H_2O = Cu(NO_2)_2.6H_2O + 92{,}900$ cal.

[2] *Proc. Amer. Acad.*, **42**, 573 (1907); *Z. physik. Chem.*, **59**, 532. *J. Am. Chem. Soc.*, **32**, 431 (1910).

by more than 1°. This is worthy of mention because in this neighborhood the heat capacity of water changes by about 0.02 per cent. per degree. However, since the metal portions of the system have a larger temperature coëfficient of opposite sign, the effect of the changing heat capacity of water is at least partially neutralized.

CANE SUGAR.

No.	Weight substance in air. Grams.	Observed rise corrected for bare protruding thread and stirring.	Correction for iron wire burnt.	Correction for HNO_3 formed.	Corrected rise.	Rise per gram substance.	Deviation from mean. Per cent.
1	2.4994	2.909°	—0.008°	—0.003°	2.898+°	1.1596°	+0.05
2	2.5018	2.908	—0.006	—0.004	2.898+	1.1585	—0.05
3	2.4987	2.910	—0.008	—0.004	2.898	1.1597	+0.06
4	2.5004	2.909	—0.006	—0.004	2.899	1.1593	+0.02
5	2.5035	.911	0.008	—0.003	2.900	1.1583	—0.07
6	2.2743	2.646	0.007	—0.003	2.636	1.1590	0.00

Average rise per gram sugar (weighed in air) = 1.1591°.
Average rise per gram sugar (weighed in vacuum) = 1.1584°.

BENZOIC ACID.

7	1.5089	2.812°	—0.007°	—0.003°	2.802°	1.8570°	+0.02
8	1.5390	2.870	—0.008	0.004	2.858	1.8570	+0.02
9	1.5059	2.809	-0.008	—0.004	2.797	1.8574	+0.04
10	1.4467	2.698	-0.008	-0.003	2.687	1.8572	+0.03
11	1.5635	2.913	—0.008	-0.003	2.902	1.8561	—0.04
12	1.5630	2.912	—0.007	0.004	2.901	1.8560	—0.04
13	1.6584	3.090	—0.008	—0.004	3.078	1.8560	—0.04

Average rise per gram benzoic acid (weighed in air) = 1.8567°.
Average rise per gram benzoic acid (weighed in vacuum) = 1.8552°.

The internal agreement of the two series on sugar and benzoic acid indicates that the new bomb can be safely used for work involving the highest accuracy. The greatest deviation from the mean is 7 parts per 10,000 in the case of sugar and 4 parts per 10,000 in the case of benzoic acid. This is probably as close an agreement as can be expected from a mercury thermometer and, indeed, it compares very favorably with the best work with electrical thermometers.

The results described in this paper are not absolute, but are purely relative. Therefore, it is interesting to compare the ratio of sugar and benzoic acid. The ratio resulting from this series (vacuum weights) is 1.6014. A similar comparison of a very high order of accuracy has been made by Emil Fischer and Wrede.[1] They have made two series of determinations on benzoic acid. The ratio from their first and most concordant series is $\frac{26.478\text{Kj}}{16.545\text{Kj}} = 1.6003$; that from the average of the two series is $\frac{26.472}{16.545} = 1.6000$; while the ratio from their three highest determinations of benzoic acid is 1.6008. The differences between these ratios and that found in this paper are respectively 0.07 per cent., 0.09 per cent., and 0.035 per cent. The value of the ratio found by the Bureau of Standards is 1.6016.[2] The agreement here is even more satisfactory; in fact, it is identical within the possible experimental accuracy. In spite of the concordance of their ratios the absolute values assigned by Fischer and Wrede and the Bureau differ by a quarter of a per cent. The reason for this discrepancy is not apparent at present.

UNIVERSITY OF ILLINOIS,
URBANA.

ADDRESSES

THE LATEST ACHIEVEMENTS AND PROBLEMS OF THE CHEMICAL INDUSTRY.[1]

BY CARL DUISBERG

Probably in no domain of human knowledge and endeavor have the combined forces of theory and practice, intimately acting and reacting upon each other, made such immense strides and led to the solution of such difficult problems as in the Chemical Industry, an industry which, indeed, had its beginnings in the distant past, but in its vast development and international character is essentially a child of modern times. Success has so emboldened this industry that it considers itself capable of solving any problem, provided the men in its service are well trained in theory and practice and ready to devote themselves to the best of their ability, with patience and perseverance, to the object in view. This has been shown by the struggle between the contact process of producing sulfuric acid and the old "chamber process," by the rivalry between the Solvay process and the Le Blanc method in the manufacture of soda; by the production of nitric acid and its salts by direct oxidation of nitrogen of the air under the influence of the heat of the electric discharge; by the manufacture of ammonia from atmospheric nitrogen indirectly *via* calcium cyanamide, and directly by combination with hydrogen; by the replacement of madder by alizarine, and of natural by synthetic indigo, as well as by innumerable other instances in the color, perfume and pharmaceutical industries.

If I venture before an audience not wholly consisting of chemists, within the brief period of an hour, to describe the latest achievements of the chemical industry and to recount the problems that are engaging our attention, I must restrict myself to a great extent both in the choice of the subject matter and its mode of presentation. We can, indeed, merely touch upon the most important happenings in our industry and must, from the very outset, refrain from a thorough discussion of the subject, either from the purely chemical or the technical side. However, what cannot be described for lack of time, and what we should very much like to add for the sake of those chemists who are present, is illustrated by our rich collection of diagrams, products and materials of all kinds. What can neither be mentioned in my paper nor illustrated by these exhibits, will be demonstrated by means of lantern slides, and, should you possess patience enough, I shall show you at the conclusion of my address one of the newest factories which the German Chemical Industry has

[1] General lecture by Geheimer Regierungsrat Prof. Dr. Carl Duisberg, Managing Director of the Farbenfabriken of Elberfeld Co. Eighth International Congress of Applied Chemistry, New York, September, 1912.

[1] *Sitzber. K. Acad. Berlin*, **19, 20, 21**, 687 (1904); *Z. physik. Chem.*, **53**, 161 (1903); **69**, 218 (1909); **75**, 81 (1910).

[2] Private communication from Dr. W. F. Hillebrand.

built on the Rhine, with its various manufacturing departments and, above all, its provisions for the welfare of its employees.

In the spirit of Faust, "Who brings much will bring something to many," I invite you to make a flight with me in an airship, as it were, over the fields where the Chemical Industry holds sway and, from our point of vantage, to take a bird's-eye view of the latest achievements of this industry. Now and then, we shall make a landing and examine the most attractive features a little more closely.

Production of Power.—The question of power, which is of the utmost importance in every industry and especially in the great synthetic processes by means of which nitric acid and ammonia are manufactured, is now dominated by the perfected utilization of hydraulic power and the development of the turbine. Not only does the transmission of electric energy render it possible to utilize water power at great distances, but it also permits the transmission of power evolved at the coal mines and the peat fields to distant points, thus eliminating the necessity of transporting the fuel itself. Recently, we also learned to apply the principles of the water turbine to the steam turbine. But this advance over the piston steam engine, which Watt so ingeniously constructed about 150 years ago, has already been surpassed by benzine, petroleum or oil motors (Diesel motors), and, above all, by the reliable gas engines which are driven by blast furnace gases, Mond gas, and, more recently, by peat gas.

Production of By-Products.—The manufacture of by-products goes hand in hand with this more direct generation of energy from fuel. These products include ammonium sulphate, of such great importance in agriculture, and the tar distillation products so indispensable in the color industry. The latest and most rational method of utilizing the peat or turf beds, so plentiful in Germany and in many other countries, is practiced in Schweger Moor near Osnabrück according to a process discovered by Frank and Caro. There, peat gas is produced and utilized and ammonia obtained as a by-product, the required power being generated in a 3,000 H. P. central electric power station. The moorland, after removal of the peat, is rendered serviceable for agricultural purposes.

At that place, nearly 2,500–2,600 cubic meters of gas with 1,000–1,300 calories of heat were obtained from 1,000 kg. of absolutely water-free peat in the form of air-dried peat with 45 to 60 or 70 per cent. of moisture. This gas represents energy equal to 1,000 H. P. hours, equal to 700 kilowatt hours, after deducting the heat and power used for the operation of the gas works. In addition 35 kg. of ammonium sulphate were produced from the above quantity of peat which contains 1 per cent. of nitrogen.

The greatest problem of power production, the direct conversion of coal into electric energy by means of gas batteries, a problem which we had hoped to solve 25 years ago, is still to-day nothing more than a dream.

Production of Cold.—Besides the problem of power and heat, the question of refrigeration is one of growing importance to the chemical industry. Instead of the ammonia machines with which a temperature of −20° C. can be attained, we employ to-day sulphurous acid machines or, better still, resort to the carbonic acid gasifier which yields a temperature of −40° C. It is hoped in the near future to produce refrigerating machines, which, by the use of suitable hydrocarbons, will give temperatures of −80° C. Plants for the liquefaction of air, producing as low a temperature as −190° C., are becoming more and more common and are especially profitable where gas mixtures, rich in oxygen, or where pure nitrogen, which is simultaneously produced, can be utilized. Diagrams showing the process invented by Linde for the rectification of liquid air with the object of isolating nitrogen and oxygen are exhibited here. The Badische Anilin and Soda Fabrik in Ludwigshafen on the Rhine intends to manufacture hydrogen from water gas in a similar way and to utilize the carbon monoxide, which is simultaneously obtained, as a source of power. In a large plant which is being erected, the firm is going to produce ammonia synthetically by combining, according to Haber's invention, pure nitrogen, obtained by the liquefaction and rectification of air, with hydrogen manufactured as above. Particulars about this process will be given during the Congress by Professor Bernthsen in his lecture on "Synthetic Ammonia."

Size of Apparatus.—Influenced by the Solvay process for the manufacture of soda and its pecuniary advantages, the apparatus used in the chemical industry have enormously increased in size. In this respect the United States, no doubt on account of the example set by the iron industry with its blast furnaces with a daily capacity of 500 tons, its giant conveyers (50-ton wagons), its huge hoisting cranes, is ahead of other countries. But careful calculations have proved that there is a limit in this direction. The failure, on account of size, of the Mactear sulfate furnace, with a daily output of 25 tons, is well known, while the mechanical sulfate furnace of the Verein Chemischer Fabriken in Mannheim, which produces only 7 tons a day, is a success everywhere. It is not improbable that the high cost of construction and the great loss which accidental stoppage entails will necessitate a reduction in size of the wonderful Wedge furnace, a creation of the United States, which roasts 30 tons of iron pyrites per day.

In the organic chemical industry, the iron vessels for chlorination, sulfonation, nitration, reduction and oxidation, as well as the wooden tanks in which we diazotize and produce colors, have developed from the small vessels and vats of former years into apparatus of mighty size, their limit being generally determined by the capacity of the mechanical industry. But here, too, the mistakes which often occur in manufacturing processes and the extra losses which they involve, teach us that a wise moderation should be exercised.

Wherever possible, continuous operations have replaced those processes which worked intermittently. In this way loss of time and expense, caused by cooling and reheating, are avoided. This is exemplified by Uebel's new method of the production of nitric acid from Chili saltpetre with retorts lying above each

other and without stirrer, and by that of the Badische Anilin and Soda Fabrik, where the chambers are back of each other with stirrer, these methods having replaced the old single retort process.

MATERIALS FOR APPARATUS.—As regards materials for chemical apparatus several new wares must be referred to:

Quartz.—Apart from the fact that the saltpetre industry of Norway taught us how to absorb dilute nitrous gases in towers 20 meters high, made of granite, a substance which was rarely used for chemical purposes, we have to-day at our disposal tubes, dishes and vessels of fused quartz, which are stable against acids and heat and which are manufactured in the same sizes and dimensions as the well known earthenware vessels.

Refined Steel.—The greatest progress, however, has been made in the manufacture of iron alloys or refined steel.

Thanks to the kindness of Friedrich Krupp, of Essen, I am in the fortunate position to describe a large number of hitherto unknown substances of great importance, of which I exhibit magnificent specimens, photographs, and lantern slides. Just here, however, I must ask you to make one of the landings from the upper air and permit me to deal with the subject at greater length. You will be astonished at the immense progress which has been made to the general benefit of our industry.

Of the greatest interest are the alloys of iron with other heavy metals and metalloids, *i. e.*, alloyed steel.

Instead of carbon, other elements are employed, which likewise enhance the hardness of steel, but prevent the formation of a crystalline micro-structure liable to cracks and flaws. The most important of these elements is nickel.

Nickel Steel.—The readiness with which nickel forms an alloy with iron has long been common knowledge. Even in Bessemer's days, attempts were made in Great Britain to turn out cannons made of steel containing 2 per cent. nickel. The experiments were not successful because the nickel obtained at that time contained impurities, such as copper, arsenic and sulphur, so that the steel could not be forged. Thirty years later pure nickel, as we know it to-day, made successful results possible. The same was the case with chromium, silicon and manganese, and not until these elements were produced pure, could successful alloys be manufactured with them, either alone or together with nickel. The chief aim in the manufacture of these alloys is the formation of an amorphous, pliable structure of the steel. This result is attained not only by removing more or less carbon, but above all by a certain thermic treatment, namely, by suddenly cooling steel heated to a high temperature, heating again and keeping it at a certain lower temperature. Here you can see two samples of steel; in the one case, the coarse crystallization of the pure carbon steel before it is forged, and in the other, the same steel refined by the thermic treatment. The difference in the micro-structure of the forged carbon steel and that of the forged and thermically treated nickel steel must also be noted. While carbon steel after forging still shows a crystalline structure with visible cleavage planes of the crystals, the section of nickel steel displays an amorphous structure closely resembling that of welded iron. For comparison sake, a sample of a welded iron fracture is exhibited. It must not be overlooked, however, that nickel and chrome-nickel steels are twice or three times as hard as welded iron. There are also exhibited test pieces of alloyed steel construction parts to be used in the automobile industry. Notwithstanding the high tensile strength of about 90 kilos per square millimeter (*i. e.*, about 55 tons per square inch), no fracture is noticeable although they are greatly bent.

Aside from these improvements, which are of such great moment for structural steel, the iron alloys have found many new applications.

I merely mention the different nickel alloys for shipbuilding, electric appliances, and for valves. These valuable alloys containing 23 per cent. and more nickel, are non-magnetic, and not affected by atmospheric influences; those containing 30 per cent. nickel possess great resistance to electricity, while the coefficient of expansion of steel with 45 per cent. nickel is only one-twentieth of that of ordinary steel and not greater than that of glass.

Chromium, Tungsten and Molybdenum Steel.—It is a very interesting and novel fact that by the thermic treatment alone the micro-structure of the cheaper kinds of unalloyed iron plates and iron shapes is so changed that it becomes three times as resistant to the destructive effect of acids. If alloys of iron with chromium, tungsten, molybdenum and aluminum in certain proportions are thermically treated, this resistance is increased five-fold, as is shown by samples of ordinary carbon steel and chrome-nickel steel which underwent a treatment with dilute sulfuric acid for 56 days.

An alloy of ordinary iron with 5 per cent. nickel is an excellent material for withstanding hot caustic soda. Most astonishing properties are displayed by steel alloys containing more than 10 per cent. of chromium and a small addition (2–5 per cent.) of molybdenum. Such alloys are manufactured in the form of malleable cast and forged iron pieces by Krupp according to the patents of Borchers and Monnartz in Aix-la-Chapelle and in the form of rolled tubes by the Mannesmann Röhrenwerken in Remscheid. These alloys are insoluble not only in dilute hydrochloric acid and sulphuric acid, but also in dilute nitric acid, even with the addition of alkali-chlorides, and if they contain about 60 per cent. chromium, 35 per cent. iron, and 2–3 per cent. molybdenum they withstand even boiling aqua regia. You see here samples of this extraordinary steel, after treatment with acids, compared with ordinary steel and cast iron.

Tool Steel.—It must be especially mentioned that the alloys of iron with chromium, tungsten and molybdenum tempered by a special process invented by two Americans, Taylor and White, find most important uses as quick turning steel for all kinds of tools.

Vanadium Steel.—The most recent improvements in

the manufacture of steel for tools which must of necessity keep pace in hardness with structural steel have been made by the employment of vanadium. Unfortunately, this metal whose use is steadily increasing is still very dear, and the chemists' problem is to produce it more cheaply. If the price could be reduced perceptibly, metallurgists prophesy a great future for this metal, which exercises a very favorable influence on the micro-structure of steel.

Of great importance are those alloys of iron with chromium, tungsten and vanadium which possess a high degree of hardness even at 400°–500° C. They are needed by engineers for the construction of steam turbines and for the embossing and spraying of metal objects heated to redness, a process which has lately found extensive application. Chemists use these kinds of steel whenever chemical reactions are carried out at high temperatures and pressure, *e. g.*, for the synthesis of ammonia according to Haber's process.

The very latest alloy has now been patented and is being manufactured by Krupp for the construction of safety vaults and safes. This steel can neither be drilled nor exploded, nor can it be cut by the oxy-hydrogen flame.

Two samples of steel are exhibited, one of ordinary steel in which great holes have been cut in $5^1/_2$ minutes by using an oxy-hydrogen flame and in 6 minutes by an oxy-acetylene burner, and a specimen of this new alloy which has remained intact after being treated with the same oxy-hydrogen and oxy-acetylene flames for $1^1/_2$ hours. Let us hope that on this hard and infusible material the scientific safe-burglar will exercise his noble art in vain.

Manganese Steel.—Of the alloys made with manganese, the manganese steel or hard steel, first produced by Robert Hadfield, because of its great wearing qualities, is chiefly used for cast iron parts of disintegrators and rails of electric tramways. On account of its hardness, this steel is not malleable, but it can be bent in the cold state and is thus very safe against breaking. It is therefore of much interest to the chemical industry where, in almost all branches, grinding operations are carried out.

Silicon Steel.—Finally, I wish to refer to alloys of iron and silicon which contain 1.5–2.5 per cent. silicon and a high percentage of carbon. This steel is excellently adapted for tools and springs which must stand high strain. Since steel alloys containing much silicon, although brittle and porous, have proved very stable against acids, they are now being used more and more where such a property is of importance.

Alloys with about 4 per cent. silicon, but very poor in carbon, are of greater value than the above. Robert Hadfield first pointed out the importance of this alloy, while Krupp, working in connection with Capito and Klein, a firm of fine-plate rollers in the Rhineland, considerably improved it and introduced it for electric purposes. It is employed in large quantities in the form of sheets of 0.35 mm. ($^1/_{70}$ inch) thickness for the construction of dynamos, alternate-current motors and transformers. In Germany alone, the consumption of this alloy already amounts to 8,000 tons a year. This material has a resistance to electricity 4 or 5 times greater than that of ordinary iron and loses only half as many watts, so that the injurious Foucault currents are reduced to a minimum. The manufacture of transformers has therefore become much cheaper, for the proportion between iron and copper is much more economical. The production of this silicon iron alloy with its very low percentage of carbon, and that of the chrome-nickel steels almost free from carbon, became possible only after silicon and chromium, entirely free from carbon, could be manufactured by electric smelting processes.

Electro-Steel.—Since the electric smelting furnace has come into use in the steel industry, the problem of removing sulphur, which engaged the attention of chemists for so many years, has been solved. It has been found that the electric furnace process produces a slag free from metal, and such a slag is the prime requisite for the complete desulphuring of the steel bath.

Electrolytic Iron.—Superior to the silicon steel, poor in carbon, in its electric properties the "Ideal" metal for electromagnets, is the pure electrolytic iron—first produced by Franz Fischer, of Charlottenburg, and now manufactured by the firm Langbein-Pfanhauser & Co., Leipzig. Formerly it was impossible to produce it free from hydrogen, consequently it was hard and brittle and was not malleable. Only by electrolyzing at 100°–120° C. and employing an iron salt solution mixed with hygroscopic salts, such as calcium chloride, the iron became free from hydrogen. Its hardness then sinks far below that of silver and gold and is not much greater than that of aluminum. It possesses the valuable property of becoming magnetic more quickly than ordinary iron containing carbon or silicon, and also of again losing its magnetism more readily, thus considerably increasing the efficiency of electro-motors for which it is used. Among the exhibits, you will find several objects made of this electrolytic iron; for example, a cathode made from an electrolytic iron plate during 5 days of uninterrupted operation; also plates made by rolling; further a motor which, if constructed of silicon iron, would furnish 0.5 H. P., but being composed of electrolytic iron, though in use for several months without appreciable signs of wear, it now furnishes 1.3 H. P., in other words, it is $2^1/_2$ times as efficient.[1]

With all these new materials at our disposal, among which I must also mention copper, with 10 per cent. silicon, and copper nickel, we shall surely be able to improve all sorts of chemical apparatus that suffer so much from wear and tear.

After this short invasion of the domain of metallurgy, we shall now turn our attention to the chemical industry proper, first dealing with the manufacture of the heavy inorganic chemicals.

Sulphuric Acid.—The triumphal progress of the contact process for the manufacture of sulphuric acid in the United States scarcely has its parallel in Germany, where it originated. Platinum, in spite of the fact that its price has increased three-fold, is still our

[1] See *Zeitschrift fur Elektrochemie*, No. 16 (1909).

principal contact agent. As it is possible to carry out other contact processes with various contact materials, we shall certainly find other agents than platinum available for sulphuric acid anhydride. It ought therefore to be a fruitful field for research to find cheap substitutes for platinum. In the 20 years that have elapsed since Knietsch first successfully carried out the contact process, the Americans have increased their output three-fold for the same weight of platinum. Nevertheless, the old lead-chamber process still competes with the new method, and the steady improvement of this process and the purity of the resulting acid must be acknowledged. In fact, the lead-chamber process promises to make further progress in the future in view of the success of Falding's high chambers and Opls towers in which large quantities of acid flow down.

The Gaillard tower is supreme for concentration and recovery of the acid and for the regeneration of the various waste acids.

Ammonium Sulphate.—A new way of manufacturing sulphuric acid, together with ammonia, from the gases which are produced by the dry distillation of coal, is looming above the horizon. Burkheiser is seeking, with the aid of especially prepared wet iron compounds, to bind the sulphur, simultaneously absorbing cyan, and to convert the ammonium sulphite thus produced into ammonium sulphate by oxidation with atmospheric air.

In competition with Burkheiser, Walter Feld is endeavoring to recover sulphur directly as ammonium sulphate by a series of interesting reactions, in which thiosulphates play an important part. Such plants are in operation in Königsberg and here in New York.

Nitrogen Compounds.—So much has been written concerning the progress made in the last 5 years in the utilization of atmospheric nitrogen, that I need not enter into a description of Birkeland-Eyde's, Schonherr's or Pauling's process for the direct oxidation of nitrogen by means of the electrical discharge, nor of Frank-Caro's method of forming cyanamide from carbides [the world production of cyanamide is, according to Dr. N. Caro, 120,000 tons per year, of which 31,000 tons are manufactured in Germany (16,000 in Trostberg and 15,000 in Knapsack near Cologne), 19,000 tons are made in Niagara Falls by the American Cyanamide Co., and during the next three years the total production is to be increased to 200,000 tons], nor is it necessary to describe the Serpek process for the production of ammonia from aluminum nitrides combined with the utilization of alumina which is simultaneously obtained. I will mention, however, that the problem of concentrating the dilute nitric acid, as obtained in the large absorption apparatus from nitrous gases, has been solved by Pauling's method, in which sulphuric acid is used in a battery of towers. It is also possible now to economically convert cyanamide into ammonia and this again into nitric acid.

Soda and Chlorine.—The 50-year old Solvay process, which has conquered the whole world, still remains master of the situation. This is all the more remarkable since it is still imperfect as far as the yield is concerned; a quarter of the salt used in the process is lost as such and the whole amount of chlorine in the form of calcium chloride.

Although the materials employed in the LeBlanc process are completely utilized, this fact will not give it any chance of surviving, and it would seem to be now chiefly of historical interest.

Not less remarkable is the 25 years' career of the alkali-chloride electrolysis. The limited market for chlorine compounds and the great space taken up by the electrolyzing baths were great obstacles to the progress of this apparently simple method. For the same reasons the most approved processes, such as the Griesheim cement cell, the quicksilver cathodes of Castner and his successors, the Aussig Bell and the wire-gauze diaphragm of Hargreaves, with its many varieties, of which the Townsend cell is the latest and best, did not develop as expected. The limited demand also quickly restricted the operation of the brilliant method of manufacturing chlorates by electrolysis.

Tin.—Tin is not only produced from natural ores, but also in more than 20 detinning establishments from tin-plate and tin-can waste; 200,000 tons of tin-plate waste are subjected to this treatment and about 24 million Marks ($6,000,000) worth of tin and iron are recovered. The electrolytic detinning process, on account of high wages, the great cost of current, and the considerable manufacturing loss, has been replaced—where there is a market for chloride of tin—by the patented process of Thomas Goldschmidt, of Essen. This process takes advantage of the properties of chlorine gas, in the dry state, to greedily take up tin without reacting on iron if certain temperatures are observed. Instead of the inferior quality of electrolytic tin mud, which must be converted into marketable tin by costly smelting operations, the new process yields an anhydrous tin chloride used in large quantities for weighting silk. The detinning with chlorine is not carried out with cuttings, as in the electrolytic process, but with waste pressed in hard packages so that 20 times as much material can be treated in the apparatus at the same time. In the United States this process is operated by the Goldschmidt Detinning Company of New York.

Reducing and Oxidizing Agents.—One of the most brilliant successes in applied chemistry has been achieved by the persevering experiments of some chemists with a long neglected substance, the constitution of which had never been properly understood. The old hydrosulphite of Schützenberger, rendered stable and easily transportable in powder form as an anhydrous sodium salt or as Rongalite in combination with formaldehyde, has now become a most important article of commerce. It is chiefly used in vat dyeing and for reducing purposes in general, such as stripping dyed fabrics and as Decrolin for bleaching sugar.

Peroxides, Persulphates and Perborates.—Peroxid of hydrogen and its derivatives at present find less favor in commerce, although their future appears to be very brilliant. Recently the Farbenfabriken vorm. Friedrich Bayer & Co. succeeded in rendering

this important oxidizing agent, which easily decomposes and can be marketed only in water solution, solid and stable by the addition of urea.

This powder is in the market under the name of Ortizon, but on account of its relatively high cost is intended not so much for technical as for hygienic and pharmaceutical purposes.

The interesting manufacture of sodium peroxid from sodium and the many scientific investigations of the persalts, have not been followed by great commercial success. The persulphate and perborate, however, the latter under the name of "Persil," are being manufactured on a large scale. The reason of this failure seems to be the high cost of production.

Rare Metals.—The most interesting alloys discovered by Muthmann and Auer have found little application in the arts, and the use of cerium and thorium preparations is still confined to the incandescent gaslight industry. Only the "Auermetal," consisting of 35 per cent. iron and 65 per cent. cerium, is employed and this only to a limited extent for the manufacture of pocket cigar lighters.

In the metal filament lamp industry, tungsten, which shows the highest melting point of all metals, namely 3100° C., has replaced tantalum, which melts at about 2300° C. This became possible only after successful experiments to render the metal ductile by hammering.

The elements cadmium, selenium and tellurium are obtained in great quantities as by-products; the first is produced in the zinc industry and the other two from the Tellur gold ores found in Cripple Creek, Colorado. Although sold at relatively low prices they find but little use in the industries.

Artificial Precious Stones.—Finally, I will, in but a few words, touch upon a new industry, *viz.*, the synthetic manufacture of precious stones from alumina with additions of chrome oxide, iron oxide or titanic acid. Artificial rubies and white, yellow and blue sapphires, which cannot be distinguished from natural stones, are being manufactured in great quantities in Paris and recently also by the Electrochemische Werke, Bitterfeld. They are used extensively for jewelry and especially as bearings in watches and measuring instruments.

All this will give you a striking picture of the development of inorganic chemistry which is taking a more and more important position beside organic chemistry.

Applied Organic Chemistry.—In the organic chemical industry the reactions are considerably more complicated and the apparatus mostly smaller than in the inorganic industry. Here the chemist, like a juggler with his balls, gives every atom a definite position in the many thousand combinations which carbon forms with hydrogen, oxygen, nitrogen and sulphur, and there exist the most varied reactions and processes which may lead to the same result. This chemistry of the carbon compounds has been most wonderfully perfected in the coal-tar color industry, and in every factory of this branch there are hundreds of scientifically trained chemists always experimenting and daily finding new combinations possessing properties of technical value. Before these products become finished articles to be sold as colors, perfumes or pharmaceutical preparations, they must further go through a series of numerous intermediary operations, which finally lead to the marketable chemicals.

Coal-Tar.—The starting material of the important coal-tar color industry is the black tar which is obtained by the dry distillation of coal and is known to contain about 150 different chemical products, of which, aside from carbolic acid, the aromatic hydrocarbons, benzole and its homologues, toluol and xylol, naphthalene and anthracene, play the greatest part.

More recently carbazol has been isolated from tar on a large scale and has become a most important raw material for the manufacture of the color "Hydronblue" by Leopold Cassella & Co., Frankfort a/M. Hydronblue is a sulphur dyestuff distinguished by its fastness against washing and chlorine. Acenaphthen, which also occurs in coal-tar as such, is the starting material of a red vat dye "Cibanonred," discovered by the Society of Chemical Industry in Basle. It is to be regretted that hitherto no technical use has been found for phenanthrene, which is also one of the constituents of tar.

Besides carbolic acid, its homologues and the various cresols, etc., are being isolated by Dr. F. Raschig in Ludwigshafen on the Rhine. These substances are largely employed in the manufacture of explosives and coloring matters.

As long as coal gas is produced for illuminating and heating purposes and as long as coke must be used for the reduction of iron ores, tar will always remain the cheapest raw material for the manufacture of these hydrocarbons. But since it may become necessary in the future—as is already possible to-day—to use coal in a more rational way, at the same time producing hydrocarbons, the coal-tar color industry need not fear a scarcity of this important raw material, the less so as certain kinds of petroleum, *e. g.*, Borneo petroleum, contain large quantities of aromatic hydrocarbons from which the Rheinische Benzinwerke, in Reisholz near Düsseldorf, has already isolated toluene in the form of nitrotoluene in a commercial way. If, however, a still greater demand for these hydrocarbons should occur, other methods of obtaining them must be found. We shall then surely succeed in producing them synthetically either directly from the elements carbon and hydrogen or indirectly from carbide of calcium by passing acetylene through glowing tubes—a reaction which was already carried out successfully in the early sixties of the last century by Berthelot and recently by Richard Meyer. At the present time about one-quarter of Germany's annual output of coal is converted into coke, *viz.*, 20 per cent. for foundry purposes and 4 per cent. in gas works, while in England the quantities are 12 per cent. and 6 per cent., respectively.

Distillation of Tar.—The point of greatest importance in the distillation of tar is still the separation and isolation, in the cheapest possible way, of the different hydrocarbons in their purest form. The

stills have been continually enlarged, those employed to-day having a capacity of 60,000–80,000 liters (13,000–17,500 gallons). On the other hand, a continuous process, such as is possible in the bituminous coal-tar industry, has not yet been found. A large number of patents have been taken out for apparatus intended to solve this problem, but none of them have proved satisfactory in practice.

Organic Intermediate Products.—The conversion of the aromatic hydrocarbons into intermediate products necessary for the color industry is almost always carried out by treatment with concentrated sulphuric and nitric acid and subsequent reduction of the thus obtained nitro-compound by means of metals or metallic oxides and sulphides. In the production of amines, iron is the principal agent of reduction, while zinc and tin are mostly used in the production of azo-compounds. The electrolytic reduction has not proved useful for these processes.

The methods of producing nitro- and amido-compounds have been very little changed as far as chemical operations are concerned, but with the increase of their production their poisonous properties became more and more apparent and forced manufacturers to modify the processes so that they could be carried out in tightly closed vessels in order to protect the life and health of the workmen.

In Germany legislation has been recently enacted, based on the experience of the individual factories, which lays down rules and regulations for strict observance.

Several trinitro-compounds have been shown to be explosives, and, like trinitrotoluene, are now largely employed as substitutes of picric acid in the manufacture of explosives.

The introduction of oxy-groups into the molecule is mostly brought about by melting sulpho acids with alkalies, and, according to more recent methods, with alkaline earth metals, such as calcium and barium hydrates. Since chlorine, produced electrolytically, is obtainable in unlimited quantities and chemically pure, chlorine substitution derivatives of the hydrocarbons have been employed for all kinds of synthetical purposes. Many of these chlorine derivatives can not only be converted into oxy-derivatives by melting with alkalies, but, like paranitro-chlorbenzole, they also directly exchange their chlorine for an amide group when treated with ammonia or its derivatives. Colors also often change their shade when a halogen atom is introduced into their molecule and acquire more valuable properties. Chlorine has therefore proved exceedingly useful in the preparation of intermediate products and will undoubtedly become of still greater service in the future.

In the naphthalene series, the method discovered by Bucherer and Lepetit for the conversion of the hydroxyl group into the amido group and *vice versa*, employing sulphurous acid esters, has proved of great practical value. Phosgene, too, is to-day being more and more employed. Several decades ago it became an important substance for the production of the urea of paramidobenzolazo-salicylic acid, introduced into the market, under the name of "Cottonyellow," as a beautiful yellow cotton color of great fastness to light. Its principal use, however, was for the manufacture of the bright but fugitive triphenylmethane colors. It is now especially used to combine 2 molecules of aromatic compounds with free amido groups, thus producing urea derivatives, and if the starting material is an azo color, the resulting urea derivative is, as a rule, much faster to light than the original color. Imidazol, thiazol and azimido compounds of the most varied kinds are also manufactured and converted into azo colors.

In the series of the aldehydes and carboxylic acids there are no epoch-making discoveries to be recorded. Chemists still start from hydrocarbons chlorinated in the side chain or directly oxidize the homologues of benzole. Kolbe's synthesis of salicylic acid, of which large quantities are used in the color industry, is also applied at an ever-increasing rate for the production of the oxycarboxylic acids. But the direct introduction of the carboxylic group into the benzole molecule, unsubstituted by hydroxyl, is a greatly desired achievement which, however, has not yet been attained. It is also a matter of greatest importance that in substitution reactions of the aromatic nucleus we should be able to vary at will the ratio of the isomers to be formed.

Besides the biochemical production of ethyl alcohol from wood waste and from the waste liquors of the sulphite cellulose industry, I wish to mention the synthesis of organic compounds by the addition of water to acetylene. In this manner we produce in a simple way acetaldehyde, which can be easily converted into acetic acid, a very important starting material for the manufacture of numerous products.

The steady search for new raw materials and new intermediate products to be utilized in the manufacture of colors has often been crowned with success. We need only to recall the many intermediate products which have been made available for the production of vat dyes and sulphur colors and which have led to the discovery of new substances with most valuable properties. Very often new lines of research are not always based upon preconceived theoretical ideas, but are opened up by mere accident. A keen power of observation, however, is the most necessary equipment of the chemist who aims at success.

Coal-Tar Colors.—In no branch of technical chemistry has such intense work been performed as in that of the coal-tar color industry. The outsider long ago may have thought that so much had been accomplished in this field that nothing more was left to be done. The countless dyestuffs, giving all the colors of the rainbow, might well have given rise to the belief that there was already a surplus. But here the course of events was just as it generally is in life. With growing possessions, man's needs and demands also multiply. While people were formerly content to produce with coal-tar colors every possible shade in undreamt-of brightness in the simplest way, they gradually began to make more and more exacting demands as regards fastness. Not only had materials

to be dyed a pleasing shade, but they also had to be fast to washing and light. Thus new, alluring problems were submitted to the color-chemist, and his indefatigable efforts have already carried him a long way towards the desired end. Strange to say, among the public, you will frequently meet the view that artificial colors do not give fast dyeings. This is a decided error which cannot be too emphatically contradicted. To-day we can produce almost any shade with any desired degree of fastness on any kind of material, whether it be wool, cotton, silk or paper. If the dyer does not always produce such shades it is the fault of the trade which does not express its demands forcibly enough. Of course, the dyeing with fast colors entails a somewhat greater expense which must naturally be borne by the consumer.

Just at this point, before discussing the progress made in the manufacture of fast colors and in order to prevent misunderstanding, I should like to emphasize the fact that the old colors, though not as fast as those more recently discovered and though, perhaps, quite fugitive in some respects, still have a right to exist. It would be quite foolish to dye certain kinds of paper intended to be in use for only a very short time, with colors absolutely fast to light, or to dye cloth never to be washed, with expensive colors fast to washing, or, again, to treat lining, which is but slightly exposed to sunlight, in the same way as materials which must be exceedingly fast to light. Everything according to reason. For many purposes, however, the need for shades fast to light or to both light and washing is so great that it must be given every consideration. How mortifying it must be to notice shortly after you have decorated the walls of your home with most beautiful and expensive materials, that the lovely colors daily grow more unsightly, and to see a solitary patch showing up in all its pristine glory amidst a faded background when a picture or other piece of furniture is moved to another place. As it is possible to guard ourselves against such occurrences, we should certainly do so. To-day we are able to produce the most beautifully colored wall-coverings, whether of paper or of woven or printed fabrics, to meet every requirement in regard to fastness. This is proved by the large collection of all kinds of woolen and cotton fabrics (after washing and exposure to light) and especially of wall-papers, of carpets, rubber material and balloon coverings, which the different firms of the German color and dyeing industry have placed at my disposal for exhibition.

If you now inquire how chemists have been able to make such great progress, my only answer is by logical and untiring efforts along well known ways, undaunted by failures, and by diligently following any track, however faint, that gave promise of advance.

In every branch of the color industry these methods have led to faster and ever faster dyestuffs, from the multicolored benzidine colors, described as fugitive to light and not stable to washing, to the anthraquinone colors and the indigoid vat dyes. In all these classes we have gradually learned to recognize certain regularities and to accomplish certain results by systematically grouping the components and fixing the position of the substituting groups; thus we have succeeded in increasing the fastness to light of the individual chemical according to a preconceived plan.

Indigoid Colors.—The synthetic production of colors allied to indigo was stimulated by the successful synthesis of indigo which almost entirely displaced natural indigo and called the attention of both chemist and consumer in an increased measure to the advantages of vat-dyeing. The King of Dyestuffs, Indigo, now finds itself in the company of a whole series of other colors, the brome indigos, the thio indigos and alizarine indigos, the shades ranging from blue to red, violet, gray and black. Even the "purple" of the ancients has been reproduced by Paul Friedlaender, who by isolating the dyeing principle found in certain glands of the purple snail living in the Mediterranean, has demonstrated the fact that this natural color is identical with a dibrom-indigo which had been long before produced synthetically. These indigoid colors possess the same, if not better, properties than indigo itself.

Alizarine Colors.—The fastness of the alizarine colors, *e. g.*, alizarine red, used for Turkey red, was well known in ancient times. But, whereas formerly only mordant colors were considered to be fast, and consequently only these were looked for in the anthraquinone group, which led to the discovery of alizarine-orange, -brown, -blue and the alizarine cyanines, Robert E. Schmidt in 1894–1897 succeeded in finding acid-dyeing anthraquinone colors which dye every shade, rivalling the old and well known triphenylmethanes in brightness and simplicity of application and the alizarine mordant colors in their extraordinary fastness to light. I merely mention alizarine-cyanine-green, alizarine-sky-blue, anthraquinone-blue, alizarine-sapphirole, -astrol, -irisol and -rubinol. Their fastness to light is so excellent that in the famous "Manufacture Nationale du gobelins" in Paris, they have replaced the older dyestuffs for the dyeing of wool used in the manufacture of gobelins. This means a great deal if it be borne in mind that a square meter of these gobelins for the production of which an operator needs more than a year, costs, on the average, about 6,000 francs.

Indanthrene and Algole Colors.—An entirely new era began for the alizarine series when Réné Bohn in 1901, found that his new color, indanthrene, could be used as a vat-dye for cotton. This color can be dyed in its reduced state like indigo, but is far superior to the latter in beauty and brightness of shade, as well as in fastness to washing and light. Indeed, the fastness to light is so great that in this respect it must be termed indestructible.

On account of this phenomenal fastness, indanthrene blue caused chemists to look for other vat colors in the anthraquinone series. Their efforts did not remain unrewarded, and we already possess colors of this class giving every possible shade. The Badische Anilin and Soda Fabrik sell them under the name of "Indanthrene Colors," the Farbenfabriken vorm Friedrich Bayer & Co. under the name "Algole Colors." Chemically most of these vat colors belong to the ind-

anthrene type; some of them are still more complicated nuclear products of the condensation of several anthraquinone molecules; others, again, are di- and tri-anthraquinonylamines. It must also be noted that to the greatest surprise of all experts in this branch, it was discovered in the laboratory of the Farbenfabriken vorm. Friedrich Bayer & Co., that even some of the simplest acyl derivatives (-benzoyl) of the aminoanthraquinones are excellent vat colors.

Lake Colors.—We must not leave out of sight the importance of some colors of the aniline group and especially the anthraquinone group for the production of lakes for paints and pigment colors for wall paper. The alumina lake of alizarine, the so-called madder lake, with its fine shade and great fastness to light, is best known. Other alizarine colors also yield valuable alumina lakes; thus, alizarine sapphirole gives a blue lake of excellent fastness to light. But it is not always necessary to precipitate lakes. Some of the difficultly soluble vat colors may be directly employed in a finely-divided form. Thus indanthrene and algole blue already play important roles as substitutes for ultramarine for bluing higher class paper, textiles and even sugar.

The development of the anthracene colors, aside from the tinctorial progress, brought about remarkable results in pure chemical research, for example the peculiar action of boric acid and the catalytic action of quicksilver in the sulphonation processes of anthraquinone.

But in this branch of our science as well there is still much room for development. Many problems remain unsolved and new ones are continually arising. To satisfy the demand of the dyer many dyestuffs must still be synthesized.

The ceaseless efforts of the color chemist will undoubtedly bring us farther and farther along this road, and complaints about the insufficient fastness of dyed materials will be silenced at last. If this goal is to be reached, it is absolutely necessary for the consumer to support the manufacturer, and I take this opportunity to state that in the United States of America these fast colors are to-day more generally used, and found recognition and wide-spread application here earlier than in any other country.

Pharmaceutical Chemistry.—I will now deal with the progress and problems of the pharmaceutical industry in the synthetic production of medicinal drugs. This industry is the youngest daughter of the coal-tar industry and it is not long since she celebrated her 25th anniversary. Those, who, like myself, had the good fortune to stand at her cradle when Ludwig Knorr discovered antipyrin, and to guide her first tottering steps at the time phenacetin and sulfonal were brought out, must look back with a joyful heart to this period of splendid growth. Much brilliant work has been accomplished but a vast amount still remains to be done. Here we see chemistry and medicine intimately bound together, the one dependent upon the other and powerless without its aid. What an organization, what boundless intelligence is necessary and what immense energy has to be expended in order to discover a new synthetic remedy and to smooth its path through the obstacles of commerce! First, we need a fully-equipped chemical laboratory, then a pharmacological institute with a staff of men trained in medicine and chemistry, an abundance of animals to experiment upon, and finally—the latest development in this field—a chemo-therapeutic and bacteriological department equipped according to the ideas of Professor Ehrlich; all these must be in close connection with one another. Whatever has been evolved, and after much painstaking effort selected as useful, finds its way into the manufacturing department, there to be elaborate in the most minute details and brought to the highest possible pitch of perfection. Now begins the arduous work of the scientific department! Here the right sponsors must be found, here all prejudices must be brushed aside and an extensive propaganda initiated. Next, a host of clinicians and practitioners must be called into requisition so that what has been evolved in the silent workshop will be conducted on a staunch ship into the wide sea of publicity. And, finally it is the calculating salesman's turn; he must bring in enough to cover all the expenses of the innumerable experiments that have been made, if the new drug, which has swallowed so much money, is to survive and prosper. Truly, all this is a task which only too often is misunderstood and insufficiently appreciated. If, however, a great hit is made—an event almost as rare as the Greek calends—then the envious, the patent- and trademark-violator, and even the smuggler, cling to our heels and seek to rob us of our profits which, taking everything into consideration, are really not large. But despite all this, and though unfortunately opposed by druggists and physicians even to-day, the pharmaceutical industry serenely pursues its task. For besides certain economic aims, we also have ideals to strive for. We combat systematically the symptoms of disease and are the faithful auxiliaries both of the doctor and the harassed nurse. The agonizing pains of the patient we allay with narcotics and anesthetics. When sleep flees the couch of suffering, we compel it to return; fever, we banish. We destroy the minute organisms which cause and spread diseases. Thus we add to the store of what is valuable, and perfect what already exists. We also isolate the active principles of various drugs and thus assure exact dosage and freedom from undesirable or even dangerous by-effects.

In the chemical works of Germany pure chemical science receives its due. In every branch of inorganic, organic and physiological-biological chemistry we are working with an army of scientifically trained men. In synthetic chemistry, brilliant achievements have fallen to our share. Quite recently, Stolz succeeded in building up adrenalin,[1] Decker in making hydrastinin and Emil Fischer and Wilhelm Traube in producing purin bases. All of these are magnificent

[1] 1 kg. adrenalin, which is now prepared synthetically, and has been introduced under the name of "supreranin" by the Farbwerke of Hoechst, requires for its production the adrenal glands of 40,000 oxen. This product, as well as numerous other glandular preparations, is nowadays manufactured by the large American slaughter-houses themselves.

accomplishments, and many of them have been effected in the laboratories of the industry.

That even yet, as at the beginning—the antifebrin period—we must trust to chance is shown by the discovery of atophan, the latest valuable antiarthritic, which is due to a fortunate accidental observation. In the subject of the old ergot problem, research work is gradually bringing more light and makes the possibility of synthetically producing a substitute a thing of the near future. The publications on this subject show that hemostatic alkaloids possess a comparatively simple constitution. That sedatives have their place in an age when nervous disorders are so common is not to be wondered at. I need merely remind you of the new adalin which has proved exceedingly useful. Recently, Emil Fischer, the master of chemical research, to whom the pharmaceutical industry is indebted for the synthetic purin bases, *viz.*, caffein, theobromine, and theocin, as well as the valued remedies, veronal and sajodin, has succeeded, after long and fruitless labors, in elucidating the constitution of tannin and producing it synthetically. He has thus proved that it might be possible to manufacture tanning agents of all kinds artificially and has opened up a new and promising field for research.

Chemotherapy.—But a short while ago, Ehrlich drew attention to another promising branch of pharmaceutical-medical chemistry, *viz.*, the treatment of infectious diseases by chemical means. After many years' arduous labor and many thousand experiments on different animals, this master of medicine and chemistry succeeded in demonstrating that it is possible to produce chemical substances which will kill the parasites in the human body without injuring their host and that this action is a function of the chemical constitution. The new science, with its magical bullets directed only against the injurious organisms in the body but not affecting its cells, pursued its course from aminophenyl-arsinic acid (atoxyl) to diamino-oxyarsenobenzole (salvarsan). Thus a new synthetic preparation, an arsenic compound, is added to the old and highly effective remedies, mercury, quinine and salicylic acid. It is certain that we are here only at the beginning of a new development. We know already that we are able to combat not only spirochetes but also bacterial diseases, like tuberculosis. Even carcinoma and sarcoma, those growths so destructive to humanity whose cause is, however, not yet understood, can probably be influenced in a like manner by means of selenium compounds, as first pointed out by Emil Fischer. But were we to learn to cure diseases due to trypanosomes and plasmodia, what a great work we should have accomplished in the interest of humanity and social economy, for it is in the most fruitful lands indeed that these diseases, malaria and sleeping sickness, are to be found, and man and beast are ruthlessly destroyed by them. Neither salvarsan nor atoxyl are of service here, and therefore other hitherto unknown remedies must be found.

While the treatment of syphilis, with its terrible consequences, is still imperfect in spite of mercury and salvarsan, let us hope that systematic laboratory experiments with the innumerable products chemistry is able to produce from mercury and from arsenic will finally lead to complete success.

Synthetic Perfumes.—In the perfume industry the developments made since the scent of the violet was imitated with jonon, and since the successful synthesis of camphor from turpentine, are not of such nature that we need to deal with them at great length. The importance of this industry appears from its yearly turnover of 45–50 million Marks (10–12 million dollars). Here the efforts of the chemists are directed towards determining the constitution of the complex and simple natural perfumes, isolating the various products of decomposition obtained during the investigation, and finally reproducing the natural perfumes synthetically. Such results have already been achieved in the case of the odor of the rose, lily-of-the-valley and violet. Very often certain substances are needed in the compounding of perfumes which, like indole, possess anything but a pleasant smell.

Artificial Silk.—Even if doubt be expressed as to whether artificial silk (the yearly consumption of which amounts to about 7 million kilograms) still belongs to the chemical industry because it stands in such close relation to the textile industry, with its weaving and spinning machines, yet the raw materials needed for its production, such as nitro-cellulose, copper ammonia cellulose and cellulose-xanthogenate are of such importance that the chemist and engineer equally divided the responsibility in this branch of manufacture. Viscose silk from xanthogenate of cellulose, the production of which has been recently very much improved, seems to replace nitro-cellulose silk and the copper ammonia silk. This viscose silk surpasses all other artificial silks in luster and is the cheapest to manufacture, so that the apparently simplest process of all, the copper ammonia cellulose silk, cannot compete with it any more. Among the exhibits are fine specimens of this silk from the Vereinigten Glanzstoff-fabriken of Elberfeld and their factory in Oberbruch in Dremmen near Aix-la-Chapelle, including the various raw materials, wood, cellulose, alkali cellulose and the cellulose-xanthogenates produced by treatment with bisulphide of carbon and the viscose solution itself.

Acetylcellulose. *Cellit Films.*—From acetylcellulose soluble in aceton, called cellit, the Farbenfabriken vorm. Friedrich Bayer & Co. first produced cinematograph films, but although they have the great advantage over those manufactured from nitro-cellulose of being non-inflammable, it has not been possible to introduce them generally. In all their properties the cellit films are equal to the old inflammable ones, yet the proprietors of moving picture theatres do not take them up because they fear the competition of the schools and the home where the cellit films would be largely used on account of their non-inflammability. The only help then would be such action by those in authority as to make it difficult to employ inflammable films and to facilitate the use of cellit films. There are prospects of such legislation at least in Germany, which would put an end to cinematograph fires with their great danger to life and property.

Non-Inflammable Celluloid (Cellon).—The problem of manufacturing non-inflammable celluloid by mixing cellit with suitable camphor substitutes which burn difficultly or not at all may be considered as definitely solved. Eichergrün has simplified the manufacture to an extraordinary extent by showing that certain acetylcelluloses may be gelatinized in the same way as nitrocellulose. As is well known, nitrocellulose with camphor in the presence of a solvent yields a so-called "Solid solution," and even in the dried state may be easily cut or formed into sticks, tubes or threads. Cellit, when treated in exactly the same way with appropriate camphor substitutes, can be converted into "cellon," the non-inflammable substitute for celluloid. Single blocks weighing 200 lbs. are already produced on a large scale which, like celluloid, can be sawed, cut, and polished; when heated can be pressed or bent; and when subjected to steam at a high temperature can be drawn and molded. Compared with celluloid, cellon has the advantage of being more elastic, soft and ductile. It is therefore frequently used as a substitute for hard rubber, gutta percha, leather, etc. Cellon, in the form of a highly viscous, syrup-like solution, may be employed for coating fabrics, wood, paper, metal, etc., with a thick enamel-like, uniform and pliable surface. Thus patent leather, artificial leather, insulators, balloon covers, etc., may be produced. In France this varnish is already employed for enameling aeroplanes. Objects made of this novel and widely useful material are to be found among the exhibits, being manufactured by the Rheinisch-Westfälische Sprengstoff Actien Gesellschaft in Cologne and the Société Industrielle de Celluloid in Paris.

Rubber.—Finally, I will refer to one of the greatest successes and yet one of the most difficult problems of the chemical industry, *viz.*, the production of synthetic rubber. I am proud of the fact that its production was successfully accomplished in the works which are under my management, and that I was able to follow every stage of this important discovery. Perhaps you would be interested to hear, although it is getting late, how the whole thing happened, especially as much that is untrue and misleading has appeared in the press during the last few weeks.

But first a few words about natural rubber. The old world owes its knowledge of this substance to the new. This wonderful product became known in Europe shortly after Columbus discovered America. If I, coming from across the ocean, now bring you this colloid prepared there synthetically, I merely repay part of the debt which we owe America.

Hardly a generation ago, the southern part of this great American continent furnished the whole supply of the different kinds of rubber. Since then extensive plantations of rubber trees have been established in various tropical countries and their yield has grown so enormously that the old home of wild rubber will soon be thrust into the background. This is a matter which involves many millions; consequently a very serious economical problem confronts South America.

You all know that caoutchouc is made from the milky sap of numerous species of trees and shrubs and the grotesquely formed lianas by various coagulation processes, and that this product, on being suitably treated with sulphur or sulphur compounds, *i. e.*, by vulcanization, acquires its valuable and characteristic properties. The synthetic method took quite a different route. By breaking up the very complex molecule which rubber doubtless possesses, by pyrogenetic processes, *i. e.*, by dry distillation, a veritable maze of all kinds of gases, oils and resins was obtained, as well as a colorless fluid resembling benzine, to which the investigators gave the name "Isoprene." It was the French scientist Bouchardat who first expressed the belief that this isoprene, which is obtained in very small quantities and in an impure form by the dry distillation of caoutchouc, might be closely and intimately related to caoutchouc itself. This important question was then eagerly discussed for several decades by the scientists of all countries and opinions were sharply divided. As far back as the eighties, the Englishman Tilden claimed to have prepared artificial rubber from isoprene by treatment with hydrochloric acid. But neither Tilden nor his assistants, though they worked strenuously for years, succeeded in repeating the experiments. Moreover, numerous other investigators were unable to confirm the results. Dr. Fritz Hofmann, of the Farbenfabriken vorm. Friedrich Bayer & Co., is to be regarded as the real discoverer of synthetic rubber, for, by the application of heat, he succeeded, in August, 1909, in polymerizing the isoprene molecules into the complex rubber molecule. Somewhat later Harries discovered independently another method of arriving at the same result. Everyone is now in a position to repeat this exceedingly simple experiment himself, but in order to confirm Hofmann's results, it is necessary to employ *pure* isoprene.

The practical value of this rubber, of which many samples are among the exhibits, has been tested by the highest authorities in this branch of the industry, while Professor Karl Harries, whose unremitting labors extending over many years prepared the soil for Hofmann's synthesis, has carefully examined the chemical constitution of the substance.

Isoprene belongs to the butadienes. It was therefore to be assumed at the start that betamethylbutadiene would not hold a peculiar and isolated position among the butadienes in general. It was argued that other members of this interesting group of hydrocarbons would yield analogous and homologous rubbers on being heated. In the synthesis of products occurring in nature, there is always a possibility of producing such variations, and our endeavors to find out whether this was true in the case of rubber were crowned with success, for to-day several representatives of the new class of caoutchoucs possessing different properties are known and are being submitted to technical tests. Exact proof of the existence of the class of isomeric and homologous caoutchoucs was also first presented by Elberfeld.

To you who hear this account and see these beautiful specimens, the matter appears very simple, intelligible and clear. In reality, however, it was not so. The difficulties which have been overcome were great

indeed and those which still remain to be surmounted in order to produce a substance equal to Para caoutchouc in quality and capable of competing with cheap plantation rubber costing only 2 marks per kilo, are still greater. But such difficulties do not intimidate the chemist and manufacturer; on the contrary, they spur them on to further efforts. The stone is rolling, and we will see to it that it reaches its destination. The end in view is this: that artificial rubber may soon play as important a role in the markets of the world as does natural rubber. The consumption of rubber is simply enormous. Finished articles to the value of 3 milliard marks are manufactured every year, and the raw material from which they are made, calculated at the present market price of 12 marks per kilo, costs one milliard marks. Other tasks which the chemist has on hand shrink into insignificance compared with this gigantic problem. The laurel wreath will not adorn the brow of the wild dreamer but that of the scientist who, cool and persevering, pursues his way. The seed he sows ripens slowly, and though according to the statements in the press, all this is mere child's play and the problem has been solved. I leave it to your judgment whether this is true or not, like much that printer's ink patiently transfers to paper. I am right in the midst of this excitement. I have employed articles made of synthetic rubber, and for some time I have used automobile tires made of this material. Yet, if you ask me to answer you honestly and truly when synthetic rubber will bring the millions which prophets see in its exploitation, I must reply that I do not know. Surely not in the immediate future, although synthetic rubber will certainly appear on the market in a very short time. But I hope to live long enough to see Art triumph over Nature here also.

We are now at the end of our journey. We have flown not only over the field of Germany, but also over all other countries where the chemical industry is cultivated. We have taken a passing glance at the untiring striving for advance, the restless search for the hidden and unknown, the ceaseless efforts to acquire more technical knowledge as witnessed in the great laboratories and factories of our mighty and ever-growing industry. We shall now guide our airship into the haven whence we set out and land where our co-workers have gathered from all the countries of the earth to recount whatever progress each has achieved, and to discuss, in public and private, the problems which have been solved and those which still await solution.

This is the purpose and aim of the Congresses of Applied Chemistry, and in this way they promote directly and indirectly the interests of our industry. But they also serve another purpose—to spread far and wide knowledge of our great deeds. It is thus that they impress the importance of our science and the arts founded on it upon the public in general and especially upon those who have influence in social or official positions, so that our profession may advance equally with others, and so that the importance of the chemical industry and of those connected with it from an economic, hygienic and social standpoint may become better and better known.

That the effulgent light of this knowledge will also be diffused by the Eighth International Congress of Applied Chemistry is assured by the magnificent organization which our friends, the American chemists, have provided, the skillful manner in which the affair has been conducted, the hospitable reception which has been extended to us, not only by our colleagues but by the people-at-large, and which is still awaiting us in our tours of inspection of the flourishing industry of America, in so many respects a model for others. For Chemical Science and the Chemical Industry the following words of Schiller are beautifully descriptive: "Only the serious mind, undaunted by obstacles, can hear the murmuring of the hidden spring of Truth."

SYNTHETIC AMMONIA.[1]

By H. A. Bernthsen.

You all know that of the chemical elements that occur in large quantity on our planet, nitrogen is one which is characterized by its complete indifference to chemical attack. Berzelius already says of it: "it is difficult to recognize because it does not differ from other gases by any conspicuous property, but can only be recognized by means of properties which it does not possess." We see therefore both in science and in arts that nitrogen is frequently used when it is desired to protect bodies from chemical attack by oxygen or when the commencement of an oxidation is to be prevented. The vacuum of the thermometers in instruments which are intended for high temperatures is, as you are aware, filled with nitrogen. The storage of readily combustible liquids, such as coal-tar benzene and light petroleum naphtha, is effected by covering these bodies with nitrogen; their transport by applying compressed nitrogen. It is to the indifference of this element to chemical attack that the curious state of affairs must be attributed, that although we are dependent for all the conditions of life on compounds of this body and although we live in an infinite ocean of nitrogen, yet up to a short time ago we were not in a position to obtain nitrogen compounds from it. We were forced to cover our requirements of saltpeter for gunpowder, of nitric acid for gun-cotton and for nitration and many other applications, of ammonia for refrigerators, for instance, and so on, not by drawing upon the nitrogen of the air, but by utilizing ready formed nitrogen compounds, which ultimately result from the processes of plant life of earlier times. On the one hand Chili saltpeter and on the other hand the ammonia liquor obtained in small proportions as a by-product in the manufacture of gas or coke from coal served to supply the wants mentioned. We were also and in particular dependent on these two sources of nitrogen for the requirements of agriculture, which are far greater than all the other taken together.

[1] Lecture by Herr Hofrat Prof. Dr. Heinrich August Bernthsen, Managing Director of the Badische Co., Ludwigshafen-on-Rhine, Germany. Eighth International Congress of Applied Chemistry, New York, September, 1912.

But now, while the requirements of nitrogenous manures are constantly increasing, in order to guarantee to the inhabitants of the world sufficient harvests, we have in all probability to reckon with a comparatively rapid diminution of the supply of natural Chili saltpeter. On the other hand we cannot expect the balance to be maintained by a rapid increase in the production of ammonium sulfate, for this is dependent on the manufacture of gas and of coke, which increases but slowly. To this, some working up of peat may be added, but a production of ammonia in this way as the main object of manufacture is impossible. The problem of the conquest of elementary nitrogen, of forcing this obstinate scamp into the service of our civilization, has consequently attained immediate importance for some time. Already three years ago at the Seventh International Congress of Applied Chemistry in London, I therefore had the honor of reporting on the utilization of atmospheric nitrogen and a new way for the production of nitrates from the air.

It might appear that the American continent, which is so richly blessed with the treasures of nature, can perhaps await with greater patience the development of events than could most European countries. For while the soil of the latter has been worked to the uttermost through centuries of agriculture, the unexampled development of this country has been caused, to a great extent, by the fact that agriculture had virgin soil at its disposal wherever it developed. There may still be places, such as the English poet Browning sings of:

"Nature frames
Some happy lands, that have luxurious names,
For loose fertility; a footfall there
Suffices to upturn to the warm air
Half-germinating spices; mere decay
Produces richer life; and day by day
New pollen on the lily petal grows,
And still more labyrinthine buds the rose."

In general however a change is occurring. The soil of the eastern states, if it is to yield full harvests, in the future already requires the addition of manures above all of the nitrogenous manures, for lack of the latter is most quickly noticed by the plants. A similar treatment would further be of great advantage in many parts of the southern cotton states. Finally, in the course of years, the same requirements will be noticed in the west more and more, as the development of hitherto uncultivated land even there hardly comes any more into consideration. Nature will only continue to shower her favors on man if he adapts himself with reason to her immutable laws, as expressed by the poet:

"Nur der verdient sich Freiheit wie das Leben,
Der täglich sie erobern muss."

I therefore count upon your interest if I deal to-day in some detail with the nitrogen question, and announce to you some of the progress that has been made since the last Congress.

The three methods employed for the fixation of nitrogen are: *first*, the direct oxidation of nitrogen of the air forming nitric acid, nitrates, etc.; *second*, the synthesis of ammonia from nitrogen and hydrogen; and *third*, the fixation of nitrogen to metals or metalloids and, if desired, subsequently decomposing the resulting products, nitrids, etc., producing ammonia. Three years ago it was the first of these ways with which I dealt principally. I was in a position to announce that in the processes of Birkeland of Christiania, on the one hand, and of Schönherr and the Badische Anilin- & Soda-Fabrik, on the other hand, two important ways had been opened up for oxidizing the atmospheric nitrogen with the aid of electricity obtained from water-power. Two companies had been formed by a Norwegian-French group, the Norsk Hydro Elektrisk Kvaelstofaktieselskab, and a German group, the Badische Anilin- & Soda-Fabrik together with the Farbenfabriken of Elberfeld and the Actiengesellschaft für Anilinfabrikation of Berlin. These undertakings and some other associated enterprises have in the meantime been developed with great energy and the factory at Saaheim, which converts about 120,000 H. P. of the Rjukan fall into oxids of nitrogen, is now in full swing. The management of these works has passed into the hands of the Norwegian-French group by an arrangement with the German group.

The processes for the combination of nitrogen with metals, etc., producing metallic nitrids, cyanamids, and the like, and from these ammonia, have also progressed.

On the one hand the nitrolim obtained for instance by the union of nitrogen with calcium carbid, which is produced in several factories, is in part utilized directly as manure; in part a beginning has been made with the manufacture of ammonia from it by treatment with steam. On the other hand the nitrids, and especially those of aluminum and silicon, have been more closely studied. The process of Serpek for the production of aluminum nitrid has been developed by the Société Générale des Nitrures on a manufacturing scale in order to obtain on the one hand, pure alumina for the production of aluminum, and on the other, ammonia. Then again the Badische Anilin- & Soda-Fabrik in following up its work on barium cyanid from nitrogen, barytes and carbon took up the study of the production of titanium-nitrogen compounds and that of silicon nitrid from silica, nitrogen and carbon, and then in connection with this the production of mixed nitrids of silicon and aluminum, and of aluminum nitrid itself. In this field of work also an arrangement has been made between the firms working it, the Badische Anilin- & Soda-Fabrik having assigned their patents to the Société Générale, retaining for themselves certain rights of preparing the nitrids in question according to the patents of both companies. It is to be expected that this branch of industry will also develop satisfactorily.

I refrain from discussing any of these methods of fixing nitrogen and refer to the communications made by the inventors themselves and in particular to the

lecture delivered a few days ago at this Congress, by Dr. Eyde, the general director of the Norwegian companies referred to.

I propose to deal to-day however, from my own direct experience, with the development of the problem for the synthetical manufacture of ammonia from its elements. A few years ago the solution of this problem appeared to be absolutely impossible. It has recently been the object of very painstaking investigations by Professor Haber and the chemists of the Badische Anilin- & Soda-Fabrik, and numerous patents have been taken out with reference to the manufacture. Apart from what is already published in this way, however, we have refrained from any other announcements until we were in a position to report something final with reference to the solution of the technical question.

This moment has now arrived and I am in the agreeable position of being able to inform you that the said problem has now been solved fully on a manufacturing scale, and that the walls of our first factory for synthetic ammonia are already rising above the ground at Oppau, near Ludwigshafen-on-Rhine; this factory will be opened by the middle of next year.

Permit me therefore to explain to you the fundamental points upon which this latest achievement of chemical industry is based.

The affinity of nitrogen for hydrogen, as is well known, is so small that the two do not appreciably unite with one another either at ordinary or at a raised temperature. It has long been known that by electric sparks or by a silent discharge very minute quantities of ammonia can be formed from nitrogen and hydrogen. Also by conducting a mixture of hydrogen with nitrogen prepared in a particular way over spongy platinum, Johnson (1881) thought that he had obtained ammonia, in a quantity amounting to 0.0059 gram of NH_3 per hour. The nitrogen had been obtained from ammonium nitrite and passed through ferrous sulfate solution in order to remove nitric oxids. But nitrogen prepared in other ways did not yield the ammonia, so that Johnson assumed that there were two modifications of nitrogen. Wright (1881) proved that ferrous sulfate did not absorb all the nitrogen oxids and that the ammonia was produced by the action of hydrogen on nitrogen oxid in the presence of platinum. When using pure nitrogen he also obtained no ammonia. Baker (1883) also came to the conclusion that Johnson's statements as to the production of ammonia from its elements were mistaken. In no case could Baker notice any signs of the formation of ammonia, and he decided that hydrogen does not combine with nitrogen under the influence of heated platinum sponge.

Ramsay and Young on the other hand (1884) determined the decomposition of ammonia by heat at various temperatures. In this research, among other experiments, a mixture of dry nitrogen and hydrogen was passed through a red-hot glass tube filled with iron filings, or through an iron tube. The presence of ammonia could again not be proved. When using moist gases they noticed the presence of traces of ammonia, the formation of which they explained by the decomposition of water and the production of nascent hydrogen.

Again Perman, twenty years later, occupied himself with the question of the formation of ammonia from its elements. Upon slowly passing a mixture of nitrogen and hydrogen (1 vol.: 3 vol.) through a glass tube heated to red heat, he obtained no ammonia, and the same result was attained when the tube was filled with porcelain. But when the mixture, in a moist condition, was passed over red-hot iron or several other metals, or over asbestos, pumice, pipe-clay, etc.,[1] traces of ammonia were formed, according to Perman's statement.

The investigations entered upon a new phase when Haber, armed with the weapons of modern physical-chemical methods, attacked the problem of the estimation of the ammonia equilibrium in 1904 in conjunction with van Oordt.[2] These investigators showed that at a temperature of about 1000° C. decomposition of ammonia into its elements was almost, but not quite, quantitative (of 1000 molecules of ammonia 999.76 were decomposed at a temperature of 1020° C.), and that consequently from these elements and under the same conditions very small quantities of ammonia were formed. The authors used as contact material, iron prepared from iron oxalate by heating to red heat in a current of hydrogen, and the iron was spread out upon purified asbestos. Further, for some experiments nickel was precipitated from nickel nitrate upon pure silica. From a mixture of nitrogen and hydrogen corresponding to 100 parts of ammonia they obtained at the temperature mentioned about 0.02 parts of ammonia, and even this figure was subsequently, by more accurate examination (see below), shown to be still too high. In a further publication in 1905,[3] these results were confirmed and summarized in the following statement: at the temperature of commencing red heat and upwards, no catalyzer is capable of producing more than traces of ammonia. The work was carried out at ordinary atmospheric pressure "for practical reasons," and it was pointed out that even under considerably increased pressure the position of the equilibrium would remain very unfavorable. Manganese was also taken into consideration as a catalyzer, but its effect, as also that of nickel, was less satisfactory than that of iron.

While Haber in company with Le Rossignol[4] pursued this line of research, Nernst communicated the results of similar investigations to the general meeting of the German Bunsen Gesellschaft at Hamburg in 1907.[5] He was induced to take the matter up by the fact that Haber's figures showed a remarkable discrepancy from the equilibrium figures calculated according to the famous "heat theorem" of Nernst

[1] The action of these latter bodies was explained by the presence of iron in them, but it may be stated that the alleged action of asbestos, pipe-clay and pumice is due to a mistake.

[2] *Z. anorg. Chem.*, **43**, 111.

[3] *Ibid.*, **44**, 341.

[4] *Ber.*, **40**, II, 2144 (1907).

[5] *Zeit für Elektrochemie*, **13**, 521 (1907).

himself. In order to determine the otherwise so minute quantities of ammonia, Nernst worked under pressure, using as a rule about 50 and up to 75 atmospheres, for according to the well known laws the concentration of the ammonia increases with the pressure. These results were published more in detail a year later by his co-worker, Jost.[1] The latter used as catalysts besides platinum foil or iron (prepared from iron oxid in a current of hydrogen) also manganese (obtained from an electrically prepared amalgam by driving off the mercury in a current of ammonia). The figures here obtained for the equilibrium were still lower than Haber's, a fact which Nernst said was very regrettable, for otherwise one might really have thought of preparing ammonia synthetically from hydrogen and nitrogen. Haber and Le Rossignol made a further publication in 1908,[2] having now made their measurements also at a pressure of 30 atmospheres. By this means, it is true, the differences as against Nernst's experiments on account of the position of equilibrium, as also the maximum percentage of ammonia obtainable at a given temperature, were not quite got over, but at all events the figures of both scientists agreed in showing that this maximum is extremely low. At a temperature of 1000° C. the volume percentage of ammonia calculated for atmospheric pressure is 0.0048 per cent. according to Haber and 0.0032 per cent. according to Jost, the corresponding figures at 700° C. being 0.0221 per cent. and 0.0174 per cent.[3] That is, at these temperatures the ammonia equilibrium is extremely unfavorable, while at lower temperatures the catalytic action of the metals in question was too low to be able to work with them.

To sum up all these investigations on the direct combination of nitrogen and ammonia, it can be said that the problem seemed now to have become more than ever a mere dream, of which the realization appeared to be quite beyond the bounds of possibility, so that there was every reason why the scientist should turn his back on so unfruitful a field.

In spite of this, Haber had a feeling that a technical synthesis of ammonia from its elements could be rendered possible, and placed himself in communication with the Badische Anilin- & Soda-Fabrik for the promotion of the work. He then showed, still in 1908,[4] that the technical preparation of ammonia from its elements can in fact be carried out, in spite of the unfavorable equilibrium and the low catalytic capacity of the contact metals used, if the mixture of nitrogen and hydrogen is kept under constant pressure during the whole of the operation and is subjected alternately to the catalytic formation of ammonia at a high temperature and then freed from ammonia by absorption or condensation at a lower temperature. Care must at the same time be taken that the heat of the reaction gases containing ammonia is transferred afresh to the gas mixture about to be acted on. In other words, the nitrogen-hydrogen mixture circulates under continuous pressure, through the vessel for the formation of the ammonia, the vessel for the separation of the ammonia and a circulating pump, all these being connected up to a closed endless circuit. Of course it is advisable at the same time to replace with a fresh nitrogen-hydrogen mixture as much of the gas as is converted into ammonia.

It was further found when working according to this continuous process of Haber's under conditions which induce a relatively high concentration of ammonia that the advantages of the heat regeneration are no longer of such vital importance, but that it is sufficient in this case to work continuously under pressure without at the same time regenerating heat.[1] Finally it was seen[2] that it is not even absolutely necessary to work continuously under pressure (that is, to circulate the gases continuously under pressure), if the reaction is carried out under very high pressure, for instance at about one hundred atmospheres, preferably however at from 150 to 250 atmospheres and even higher. A range of pressure is hereby introduced which had never been touched in the synthesis of ammonia and was also something quite new in any manufacture, for no one had previously so much as thought of carrying out technically a catalytic reaction with gas currents at the necessary high temperatures under such an enormous pressure.

By these means, under a pressure of 200 atmospheres, at a temperature of from 650–700° C. and using an iron catalyst prepared from the purest iron oxid, occupying a space of 20 cc., and with a gas speed of 250 liters per hour (measured at ordinary pressure) it is an easy matter to obtain for example 5 grams, or per liter of contact space, 250 grams of ammonia in an hour.

The following further point comes here into consideration. All previous publications had in view exclusively the determination of the ammonia equilibrium, which can be found theoretically most accurately in a steady volume of gas. If a current of gas is used, the rate of flow must naturally be kept low, so that one may be sure that equilibrium is reached. Now there were no indications as to how far the concentration of the gas would be reduced when the rate of flow is raised, and whether the concentration would be sufficient when such a rate of flow is taken as must be done when working on a technical scale. Haber has therefore rendered signal service in showing that one can work successfully with such higher rates of flow.

A diagrammatic exposition of an apparatus used by Haber is shown on the chart[3] before you. The catalyst is in a metal tube which opens in front into a heat regenerator. The gas mixture passes from behind into the metal tube, through the catalyst and then through the heat regenerator into a circulating pump. Leaving this it passes in countercurrent around the outside of the regenerator tubes and the tube containing the catalyst and then enters this in front, repeating

[1] *Z. anorg. Chem.*, **57**, 414.
[2] *Zeit. für Elektrochemie*, **14**, 181 (1908).
[3] *Z. anorg. Chem.*, **57**, 193; *Zeit. für Elektrochemie*, **14**, 193.
[4] German Patent No. 235,421, October 13, 1908.

[1] French Patent No. 406,943.
[2] German Patent No. 238,450, September 14, 1909.
[3] See the sketches in Haber's article in the *Zeit. für Elektrochemie*, **16**, 244–5 (1910); and also British Patent No. 17,951 1909.

this journey again as described. The apparatus can be protected against loss of heat to the air by packing it in isolating material and can be enclosed in an outer shell which can withstand the pressure. The whole of the circulation takes place at high pressure. The catalyst is kept at the suitable temperature by electrically heating from within or by applying heat from the outside. Between the heat regenerator and the circulating pump the gases pass through either an absorber or a condenser for ammonia. By means of a branch tube the nitrogen and hydrogen combined to ammonia can be replaced.

Finally, it was a great step forward when Haber found catalysts with the property of rapidly combining nitrogen and hydrogen to ammonia in sufficient quantity even at much lower temperatures than those previously required. He found this to be especially the case with osmium. This metal has such a very favorable action even at 550° C. and below, that under a pressure of 175 atmospheres a gas concentration of 8 volumes per cent. of ammonia can be obtained. This was all the more astonishing, as platinum, which is closely related to osmium, has but a very slight catalytic action. For use on a large scale, however, osmium scarcely comes into consideration, for the world's stocks according to Haber do not amount to much over 100 kg. and only small quantities (about 1 kg.) are obtained annually; this quite apart from its high price and very unpleasant properties.

Very soon Haber found in uranium a further very good catalyst; it can be employed in the form of the metal, of an alloy, or nitrid, or carbid. In the form containing carbon or carbid, such is as produced in the electric arc from uranium oxid and carbon, it crumbles in the gas mixture under high pressure to a very fine powder containing nitrogen, which even under 500° C. has an excellent catalytic action. No water, however, or impurities which give rise to water must be present in the gases, when uranium is used in this way. From the following table which shows the equilibria obtainable at different temperatures and pressures, can be seen the importance of the temperature at which a catalyst is active for the equilibrium of the ammonia produced.

EQUILIBRIA ($N_2 : 3H_2$).

	Pressure.	
Temp. Degrees Centigrade.	1 atm. Per cent.	100 atm. Per cent.
800	0.011	1.1
700	0.021	2.1
600	0.048	4.5
500	0.13	10.8
400	0.48	..

Haber published a short report of his work in 1910.[1] To my great regret Professor Haber has not been able to accept the invitation of the officers of this Congress to report personally here on his researches, owing to being hindered by pressure of work. I have great pleasure in fulfilling his wish and thanking the officers of the Congress to-day for the honorable invitation, and express his regret to this meeting that he is unable to be present.

[1] *Zeit. für Elektrochemie*, **16**, 244–5.

I now turn to the work of the Badische Anilin- & Soda-Fabrik on the technical development of the process. This work was of course at once taken up in 1908 after the first communications of Professor Haber, and Dr. Carl Bosch was entrusted with it. In conjunction with his colleagues and with equal energy and experience in the field of chemistry and engineering he has successfully carried out the practical application of the process.

The problems to be solved were quite new and strange and demanded the mastery of very unusual difficulties. Although working with compressed gases under pressure at very low temperatures was already known in the industry, the problem here was the totally different one of constructing apparatus which should be large enough and at the same time able to withstand the high pressure with temperatures not far from a red heat. How well founded were the doubts as to the possibility of a solution of this task can be gathered from the instance of the wrought iron autoclaves commonly used in the color industry. Here, in spite of a very low range of temperature of at most about 280° C., only pressures of from 50 to 100 atmospheres at the utmost come into consideration. But above 400° C. iron loses its solidity to a very extraordinary degree.

There is further the circumstance that the metals which come into consideration for the construction of the apparatus, and especially iron, are chemically attacked above certain temperatures by the gas mixture under pressure. Although the formation of iron nitrid from iron and ammonia, which could have been expected according to the work of Frémy and others, can be avoided, yet it is found, for example, that steel containing carbon loses its carbon at the temperatures in question owing to the action of the hydrogen, so that its capability of withstanding pressure is reduced to a minimum. It was further found, when using iron itself, that it is completely changed in its qualities, chiefly by taking up hydrogen. Again, at such high temperatures iron is pervious to quite a remarkable degree to hydrogen under high pressures. The question of materials for the apparatus therefore raised at once considerable difficulties, but at length these were more than overcome by suitable construction, details of which, I am sure, you will not expect from me to-day. The danger of serious explosions or of great sudden flames of hydrogen, if the apparatus happens to become defective, can be guarded against by setting it up in bomb-proof chambers.

Great care must naturally be taken that oxygen or air does not get into the apparatus or the piping, for at the high pressure obtaining the explosion range is reached with merely a slight percentage of oxygen. Special devices are used to watch over this content of oxygen, and immediately a definite percentage is touched the alarm is automatically raised. Besides this the proper constitution of the gas mixture in circulation is controlled by analysis from time to time.

The ammonia can be removed either by being drawn directly from the apparatus in liquid form, or an absorption agent can be suitably introduced into

the apparatus. The simplest absorbent, water, has been found to be suited for this purpose; under the pressure used a concentrated solution of ammonia is secured. Any ammonia that may remain in the gas after the bulk has been removed by one or other of these methods can be further removed by special chemical means, if it is not preferred simply to leave it in the circulating gases.

As before mentioned, Haber observed that there are contact agents which are much more active than those previously known (osmium and uranium being indeed found to be much more active than pure iron prepared from oxalate of iron or oxid of iron, platinum, pure manganese, chromium, and nickel, already at considerably lower temperatures). The Badische Anilin- & Soda-Fabrik therefore decided to study the various catalysts very minutely.

In the course of these investigations, the new fact discovered, that ammonia catalysts in general are made more active by the presence of certain foreign bodies, has proved to be of prime importance. Among these "promoters," as they have been termed, are oxids, hydroxids, or salts of the alkalies, of the alkaline earths and the earth metals, further many other substances of the most varied nature, especially other metal compounds or metals themselves. In many cases just a minute quantity suffices to raise the catalytic activity. This trait is common to all catalysts, for there is not one but its activity can be raised by these means. Care must however be taken (for reasons to be discussed later on) not to choose such mixtures that metalloids such as sulfur, selenium tellurium, phosphorus, arsenic, boron, etc., under the conditions prevailing, are incorporated in the catalyst. Similarly compounds of metals with a low melting point which are readily reduced by hydrogen and which themselves do not act as catalysts must be avoided; such metals themselves as lead, tin, zinc and bismuth must also not be added.

The promoters mentioned can be added either to the prepared catalyst or to the substances used in its preparation, or the catalyst can be prepared from such materials as already contain such additions in suitable mixture (for example magnetic ironstone). Under certain circumstances the action of these foreign bodies is specially powerful, *viz.*, if the metals, or oxids, or carbonates, or other compounds which are converted into oxids on heating, are first heated to high temperatures, preferably to melting point, and so that the resulting product consists chiefly of oxids. When proceeding in this way with metals, for instance iron, of course sufficient oxygen or oxygen-producing compounds must have access. The mass of oxids obtained as described is suitably broken up and filled into the contact stove either directly or after reduction. In this case extremely small quantities of foreign substances suffice to secure a high and continuous activity of the contact mass.

We consider the marked activity of catalysts prepared in this way to be in the first place due to the fact that the additions mentioned dissolve, on heating, in the highly heated metallic oxid or become finely divided in it, and that in this way during the following reduction a sort of skeleton, which however is hardly to be detected, is formed inside the metallic mass. This effectually prevents a diminution of the surface and therefore also of the catalytic properties of the mass.

It was then further found that good results can also be achieved with pure iron, that is to say, that we can work with it at temperatures of for example not much above 600° C., thus if the iron intended for the catalysis is prepared from the oxid or other iron compound at a comparatively low temperature, preferably not above 600° C. It can also be prepared by highly heating pure iron oxids, or pure iron in the presence of oxygen, preferably to melting point, and by reducing the mass of oxid preferably at a not too high temperature.

Also manganese, which is related to iron, gives under a specific condition good results, without the addition of foreign substances. This condition is that care be taken to free completely the mixture of nitrogen and hydrogn, before it enters the contact space, from oxygen, either free or combined, for instance as steam or water. Merely drying with calcium chlorid is not sufficient. In the case of several other catalysts too a similar careful drying has proved to be useful.

Again, it has been found that another member of the iron group, molybdenum, is by itself an excellent catalyst. Compounds of molybdenum can also be used, for instance molybdic acid or ammonium molybdate.

Under certain conditions, not published as yet, tungsten, either the metal itself or as an alloy or a nitrogen compound, has been found to be a suitable catalyst.[1]

In view of the shortness of the time I must refrain from a more exhaustive discussion of this most interesting chapter of the contact bodies. It will be quite evident from what I have said that the industry has now a number of active contact bodies for the synthesis of ammonia at its disposal, and can select from case to case the most suitable.

Another discovery of first-class importance for the industrial application of the catalysis of ammonia was the recognition of the fact that there are special poisons, so to speak, for the reaction. That is to say, there are substances which hinder or prevent the reaction, although the contact mass does not suffer a noticeable chemical change, envelopment, or destruction. In the literature there was no indication whether there were poisons at all for the contact mass in the catalytic manufacture of ammonia, or what their nature would be. In actual manufacture such contact poisons were known only in the case of the catalysis of sulfuric anhydrid and even here only when platinum was used. When employing other contact bodies, such as iron oxid, or burnt pyrites, there was nothing known of contact poisons; on the

[1] Such conditions are *e. g.*, that tungsten, or its compounds mentioned, is prepared at temperatures not much above 600° C., that they are prepared from tungsten compounds by means of ammonia, in which case there is no restriction to a temperature at about 600° C.

contrary it has even been shown that the presence of arsenic, which is a poison for platinum, has actually a favorable action when iron oxid is used as catalyst.

It has now been ascertained that some of the poisons in the syntheses of ammonia are of quite a different nature from those of the sulfuric acid process; they are for instance, sulfur, selenium, tellurium, phosphorus, arsenic, boron, or the compounds of these elements such as sulphuretted hydrogen, arsenic hydrid, phosphorus hydrid, as also many carbon compounds and certain metals of low melting point which can readily be reduced by hydrogen from their compounds, for example lead, bismuth and tin, which do not act catalytically. Oxygen-sulfur compounds, such as SO_2, which acts directly and smoothly in the sulfuric acid catalysis, are very poisonous. Extremely minute quantities of these bodies, which are almost always present even in the purest commercial products or in the so-called pure gases, suffice to render the catalysts absolutely inactive or at least to diminish their action very seriously. Thus iron, for example, prepared from ordinary iron oxid with a content of one per thousand of sodium sulfate is, as a rule, inactive. Iron containing one-tenth per cent. of sulfur is generally quite useless, and even with one hundreth per cent. is of very little use, although in appearance and when examined with the ordinary physical and chemical methods no difference at all can be detected as compared with pure iron.

The recognition of these facts gave rise to two problems:

(*a*) The preparation of contact masses free from poison or the removal of such poisons from them.

(*b*) Freeing the gases to be acted on catalytically from all contact poisons.

In order to free the contact bodies from these harmful substances, the ordinary methods for removing them can of course be applied. The contact action can also be improved by heating contact metals which are inactive or of little use, owing to the presence of contact poisons, in the presence of oxygen or of bodies yielding oxygen. Or the metals can be heated, for instance, in the presence of oxygen with the addition of suitable compounds such as bases, and the resulting products reduced. These operations can be repeated if necessary. If more of such a body as mentioned is added than is necessary, it may act not merely by removing the poisons, but promote the yield, as I have already described to you.

On the other hand it is necessary, as I remarked, to take the greatest care that nitrogen and hydrogen are free or freed completely from all contact poisons. Thus a trace of sulfur, one part per million, in the gas mixture can under certain conditions be injurious, so that even electrolytically prepared hydrogen must generally be further specially purified. The minute purification of the gases is even more important when hydrogen prepared, for example, from water gas is used. The impurities too taken up from iron piping play sometimes an important part, and impurities which get into the gases during the compression, such as machine oil, often have a harmful effect.

The best method of removing impurities from the gas mixture depends in turn on the nature of these impurities and consists, for instance, according to the case, in filtering, washing, conducting over solid absorption agents and so on. One good method is to bring the gases into contact with the material of which the contact mass is prepared at a raised temperature, before passing them over the actual catalyst. The material takes up the impurities, and must of course be renewed from time to time. The negative results of earlier investigators in the formation of ammonia when using base contact metals (Wright, Ramsay and Young, and, more recently again, 1911, Neogi and Adhicary), according to which nitrogen and hydrogen do not combine in the presence of iron, are in my opinion probably due, for the most part at least, to the use of metals or gases not free from contact poison. That previous inquirers had not the remotest idea that sulfur in the contact metal could be injurious, is evident from the fact that they passed the gases without hesitation through concentrated sulfuric acid in order to dry them. The sulfuric acid thus taken up and the sulfur dioxid often contained in it can poison even the best catalyst very speedily and render it unfit for use. Or the contact metals were sometimes prepared directly from the sulfates, although a metal sufficiently free from sulfur can scarcely be obtained by this method.

A painstaking study, for which we are indebted principally to Dr. A. Mittasch and which involved literally many thousands of experiments, has afforded an insight into the importance of substances of the most varied nature as promoters and poisons and thus a sure foundation has been prepared for a reliable continuous manufacture with a good yield of ammonia.

[Here the production of synthetic ammonia by means of two identical apparatus brought from Germany by the speaker was demonstrated in two ways:

(1) The gases from the apparatus were passed over a large bowl of hydrochloric acid when dense clouds of ammonium chloride were formed.

(2) A large cloth was moistened with colorless organic compounds that give colored products when treated with bases: the gases from the apparatus were then played upon this cloth and the result was a brightly colored American flag.]

The question has not yet been touched upon in the foregoing, how the elements nitrogen and hydrogen which are requisite for the new ammonia process can best be produced on a technical scale. Theoretically, the task would be unusually simple. If you remember that the terrestrial atmosphere according to the studies of A. Wegener and others consists of practically pure hydrogen at a height of about 120 kilometers, indeed at a height of about 70 kilometers consists of almost exactly one volume of nitrogen and three volumes of hydrogen besides a trace (about one-half per cent.) of oxygen, you will understand that all the conditions were given for an ammonia factory according to Jules Verne. For it would then merely be necessary to suck down the gases from the higher strata of the atmosphere by a sufficiently long pipe line.

For us, poor mortals, matters are not so ideally simple, for, as the poet says,

"hart im Raume stossen sich die Sachen."

Fortunately, however, there is no great difficulty in separating nitrogen from the air, either by physical means, according to Linde's process, or chemically, by removing the oxygen with glowing copper, burning hydrogen, or the like. And for the preparation of hydrogen in recent times a great deal of useful work has been done too, owing to the extensive growth of its field of application. In certain works it is at disposal in large quantities as a by-product of the electrolysis of common salt. Besides this it can be produced, for example, by passing steam over red-hot iron, or from water-gas, for instance, by separating its constituents hydrogen and carbon monoxid by cooling to a very low temperature. All the methods of preparation which come into consideration we have of course minutely examined; owing to the comparatively trifling differences in the cost of production various methods can be employed. At all events, both elements, nitrogen and hydrogen, are at the disposal of the new industry to any extent and sufficiently cheap.

CHILI SALTPETER.

Year.	Chilian export.[1]	Price[2] per ton. Marks.	Total value. mill. M.	Increase.
1900	1,454,000	162.2	216.6	1901–11 995,400 tons
1901	1,274,000	172.8		that is an annual
1902	1,379,200	176.2		average of 99,500
1903	1,457,600	178.4		tons containing
1904	1,479,100	196.2		15.5 per cent., *i. e.*,
1905	1,652,200	204.8	338.2	about 15,400 tons
1906	1,731,800	215.0		nitrogen, valued at
1907	1,653,600	214.4		19 million marks.
1908	2,052,400	193.3		
1909	2,133,900	184.5	393.7	First six months 1912
1910	2,334,000	177.6		150,000 tons valued
				at about 29 million
Jan.–June				marks as against
1911	(1,299,000[3])	. .	.	corresponding per-
1911	2,449,000	190.7	467.2	iod 1911.
1912	(1,449,000[3])			

[1] According to the figures of the Association Salitrera.
[2] Annual average Hamburg quotations.
[3] Semi-annual deliveries in Europe.

AMMONIUM SULFATE.

Year.	World production. Tons.	Price per ton. Marks.	Total value. mill. M.	Increase.
1902	543,000	241[1]	131	1908-11 329,000 tons, *i.e.*, an an-
1908	852,000	237	202	nual average of 110,000 tons,
1909	978,000	230	225	containing 20.5 per cent., *i.e.*,
1910	1,111,800	248.5	276	about 22,500 tons nitrogen
		about		valued at about 30.6 million
1911	1,181,000	278	328	marks.

[1] Quotations fob. Hull.

As the production of these elements is not confined to the presence of cheap water power, all those countries where the manufacture of calcium nitrate, owing to the want of such power, is not practicable, as for instance in Germany, are now in a position to profit by the new industry. As I remarked at the outset, there is every reason to assume that this industry will find a fruitful field of employment in America, where the demand for nitrogen-manures will soon be greater than hitherto.

It can also be regarded as certain that the development of this new industry will not take place at the cost of other branches of industry and commerce. Bear in mind for a moment the present annual requirements for nitrogen manures and their continued growth. According to the tables before you these figures reached the remarkable total of 467.2 + 326, *i. e.*, 793.2 million marks (about 190 million dollars) in 1911, and each year sees an increase. In the last few years the increased demand for ammonium sulfate amounted to about 10 per cent. The increase of production from 1910 to 1911 amounted to 69,000 tons, and from 1908 to 1911 on the average as much as 110,000 tons, or 110 million kg. valued at about 30.6 million marks (7.3 million dollars). Similarly the nitrogen requirements of the world for manure purposes in the form of saltpeter is growing. Chili exported in 1908 about 2,052,400 tons of saltpeter, and already in 1911 the figure was about 2,449,400 tons, that is an annual increase of nearly 150,000 tons valued at approximately 29 million marks (7 million dollars). Indeed the European deliveries, according to the latest reports, from January to the end of June, 1912, reached as much as 1,449,000 tons, a demand which Chili was hardly able to meet.[1] The average annual increase from 1901 to 1911 amounted to 99,500 tons. That is to say, taking saltpeter and ammonium sulfate together and reckoning only the average increases, calculated on nitrogen, we have an annual increase in production of about 38,000 tons nitrogen, corresponding to nearly 185,000 tons of ammonium sulfate.

It can thus be seen what enormous quantities of synthetic ammonium sulfate must be produced to affect the total production by as much as one year. The saying so often applicable, that

"Das Bessere ist der Feind des Guten,"

will thus probably have no meaning in this field. A peaceful development of the various new industries for the combination of the nitrogen of the air side by side is to be expected, and without encroaching at all on the previous production of nitrogenous manures, a favorable horoscope may be cast for a fortunate career for the new industry.

PROGRESS IN INDUSTRIAL CHEMISTRY.[2]

By RUDOLPH MESSEL.

At a time when the latest discovery of interest may be instantly flashed to the remotest part of the world by wireless telegraphy, and the technical press discusses every possible problem as it arises, a presidential address seems to me to be almost an anachronism. In very few cases is it possible to communicate anything not already known. Whatever issue a speaker may desire to consider is sure to have been dealt with till it is almost threadbare, and I fear that the topics I venture to bring before you must be enrolled in the latter category.

I propose to deal with some aspects of the remark-

[1] During the first six months of 1912 the production in Chili was roughly 10,000 tons less than in the corresponding period of 1911, and at the same time stocks in sight in that country receded by round 50,000 tons.

[2] Address delivered by the President of the Society of Chemical Industry at the Chemists' Club, New York, September 3, 1912.

able progress made within my recollection. The ceaseless energy with which industry has availed itself of the achievements of pure science has made possible the manufacture, on a large scale, of products, either unknown but a few years ago, or seen as specimens in scientific collections, or produced only by nature. That I shall refer to relatively very few of these triumphs of chemical research and invention and mainly to inorganic products must be evident when I mention that the period covered embraces the discovery of the aniline dyes and that of artificial rubber, as well as the invention of the first electric telephone and of wireless telegraphy.

As my recollections unfortunately go back over so long a period, I feel tempted to drag in here one which may be of interest to some of my audience, though it has no connection with the matter I propose to deal with. In 1861, when I was at school at Friedrichdorf, in Germany, my master, Philip Reis, invented the first telephone. I was present at its birth, and assisted Reis in making the mechanical parts of some of his instruments and also repeatedly in his experiments, Reis being at one end of the circuit speaking or singing, I listening at the other, or *vice versa*.

The introduction of synthetic processes may be said to be the keynote of progress of modern industrial chemistry.

One of the most fascinating compounds recently introduced into industry is *calcium carbide*, CaC_2. It had lain dormant since its discovery in 1862, by Wöhler, until your countryman Wilson and Moissan made use of the electric furnace to produce it; now its manufacture constitutes a mighty industry, close on 300,000 tons being produced annually. Serving as it does as raw material for the manufacture of calcium cyanamide, it is now the parent of numerous other products of great importance. Among these may be mentioned *acetylene*, C_2H_2, so largely used as an illuminant, and for welding and cutting metals, and I may remind you that the possibility is foreshadowed that this gas will be of use as the starting point in making other chemicals. *Calcium cyanamide*, apart from its undoubted great value as a fertilizer, is coming to the fore as a source of *cyanides*, now so largely used in extracting gold. What may be of far greater importance, it is convertible by the action of superheated water into *ammonia*, which in turn may be converted into *nitric acid* and nitrate of ammonia by oxidation with air under the catalytic influence of platinum.

I have recently noticed alarming reports in the press that the impossibility of procuring supplies of nitrate of soda from Chili in time of war may prove a serious handicap to any country in the production of explosives and powder. Considering that the quantity of nitrate of soda used for the purpose is but a fraction of that required in agriculture and that large stocks are held for this purpose almost everywhere, I cannot share the writer's fear. But in view of the fact that ammonia salts are produced by all gas works and of the many attempts to produce it synthetically, the catalytic method of producing nitric acid from ammonia may deserve more attention than it has received up to now, especially if ammonia, no matter how produced, should become a sufficiently cheap raw material.

The most interesting feature in the production of calcium is the use of pure *nitrogen*. Of the various methods of preparing the gas, that which involves fractional distillation of liquefied air seems to be preferred. We are becoming familiar in industry with the impossible, but who *could have expected* such a possibility only a few short years ago? Think of the excitement caused in the scientific world when, in 1877, Pictet and Cailletet first succeeded in liquefying oxygen. Pictet's work was then described as the most brilliant achievement in modern science. The barrier between condensable and permanent gases was broken down and the latter term was deprived of its significance; but how much work remained to be done, what ingenuity had yet to be exercised, to translate this scientific discovery into a process for the industrial preparation of nitrogen! Success has been achieved by the exertions and ingenuity of several of our greatest authorities in physical and chemical science; nowadays, every gas that is required is readily procurable in the liquefied form (Cl_2, SO_2, N_2O, CO_2, NH_3, etc., etc.) in the well known steel cylinders capable of withstanding enormous pressures.

If I have laid stress on the conversion of ammonia into nitric acid, the reason is that ammonia is obtainable locally everywhere, either as a by-product of the manufacture of illuminating gas or Mond gas and from coke ovens, and that the installation for converting it into the acid is a relatively cheap one. The numerous attempts to produce ammonia synthetically from its elements nitrogen and hydrogen or from various *nitrides*, such as those of titanium, boron, magnesium, aluminum, and calcium, can moreover only be of benefit in solving the problem. True, the direct production of *nitric acid* by means of *the electric arc* from atmospheric air may appear to be a more rational process, but so long as this industry is tied to water power, and the difficulties of transporting nitric acid as such in aluminum or iron packages be not overcome, the case seems different in my judgment, particularly in countries where water power is not available and other power as yet too expensive. It is to be remembered that to carry nitric acid safely in iron packages, about 10 per cent. of concentrated sulphuric acid has to be added, and that if one or the other of the ammonia processes under trial should make it possible to transport it as nitrate of ammonia, from which it can readily be liberated at the place of consumption, the difficulty of carriage in the event of war would still remain.

My reason for referring at such length to the production of these compounds of nitrogen is their importance in agriculture. Food the nations must have, and it seems that to this end they will require the services of the chemist more and more as population grows. The great stimulus, our medalist, Sir William Crookes, has given to the production of nitric

acid by calling attention to the near approach of the exhaustion of the deposits of nitrate of soda is well known. His suggestion to utilize Cavendish's discovery of the direct interaction of the constituents of the atmospheric air and the success, so far achieved, have often been referred to; the work done by Birkeland and Eyde, by Schoenherr, Pauling, and others, is also well known, but it gives me particular pleasure to point out that here again America was the first to attempt the realization of this great problem. The realization of the other great problem, *i. e.*, the production of *ammonia from its elements*, appears likewise on the eve of accomplishment, and I hope it will not be long before we shall have details of the manner in which it has been solved in practice, and how the great technical difficulties have been overcome. It will likewise be interesting to learn something about the relative efficiency of the various uranium and iron catalytics used, etc. If the published particulars as to temperature (about 650°) and pressure (about 150 atmospheres) be correct, the task to be solved was one of no mean order. Meanwhile, we can only offer our best wishes to the ever enterprising Badische Anilin- und Soda Fabrik.

Two of the other processes mentioned before, namely, that of the production of ammonia from *calcium nitride* and from *aluminum nitride*, are likewise most interesting, the former for chemical reasons, *i. e.*, the conversion of metallic calcium first into calcium nitride, Ca_3N_2, then by the action of hydrogen on this compound into *calcium hydride* and ammonia, the calcium hydride being subsequently reconverted by means of nitrogen into calcium nitride and ammonia—so that a relatively small quantity of *calcium* is theoretically sufficient to produce an infinite quantity of ammonia. Numerous processes have been devised for producing *hydrogen*; one of the latest is Pictet's, who splits up hydrocarbons either directly into hydrogen and carbon or by means of steam, at the melting point of iron, into hydrogen and carbon monoxide, thus materially increasing the yield.

Inasmuch as *aluminum nitride* yields on hydrolysis, together with ammonia, a particularly pure form of *aluminum* hydrate, starting from an impure raw material, it may become of great importance to the aluminum industry. I well remember aluminum and more often magnesium being made by Bunsen by the electric arc on a diminutive scale as a lecture experiment. We students used to cough violently when the white fumes which were given off began to fill the lecture room, until Bunsen, smiling pleasantly, mentioned that the white fumes were due to the ammonium chloride he had added to keep the surface of the metal bright and that ammonium chloride was an excellent remedy for a cough. The coughing then stopped. As a curiosity, bars of the metal about 3 in. by 1 in. by $^1/_2$ in. were handed round and weighed by every one in his hand; the metal was doubtless produced by St. Claire Deville's sodium process. The annual output of aluminum in 1909 was over 24,000 tons, produced electrically. Now that the problem of autogenous welding of the metal, which so long defied all efforts, has been solved, the use of aluminum for chemical apparatus has become practical; apart from its utility in handling nitric acid, the metal has proved to be of the greatest value in breweries, in the food industry, and in varnish works.

The application of aluminum as a fuel by Goldschmidt has further led to the production, by his Alumino-Thermite process, of many metals in a relatively pure form otherwise only producible by the agency of the electric current. Chromium, manganese, and molybdenum prepared by this method, besides various alloys of nickel, iron and copper with these metals or with titanium and vanadium have found a use mainly in the iron industry. The igneous process of welding rails and repairing castings by means of the Thermite process is of course known to all, as well as the use of tungsten and tantalum as filaments in electric incandescent lamps. The fact that tantalum filaments, of vastly greater strength than those formerly produced by compression of the metal in powder form, can now be obtained by drawing the metal through diamond dies will doubtless give an increased stimulus to the use of the element. The mention of tantalum may call to your mind the fact that the expression rare is fallen into disuse, as the earths once known as rare are in every-day use, and, owing to the scientific acumen displayed by Auer von Welsbach, the gas industry is now well able to hold its own against the electrical. But electricity is in evidence everywhere in our industry. It threatens to displace the furnace in the alkali works, it provides us with chlorine and the time may not be distant when muriatic acid is made electrically. We are indebted to the electric furnace for the sodium industry (with its application to the cyanide, sodium amide and other manufactures) and to the production of ferrosilicon, carborundum and graphite, for which, in the form of electrodes and lubricants, America, thanks to Mr. Acheson, remains as yet unsurpassed. The manufacture of nickel by the remarkable Mond carbonyl process should not be forgotten. This metal would appear to have some future in the elimination of carbon bisulphide from coal gas and possibly as a catalytic in other industries. We do not, however, always want to get rid of sulphur. A most original idea, successfully carried into practice by Frasch, in Louisiana, is no doubt that of liquefying sulphur in the bowels of the earth and then pumping it up.

After thus rambling through the highways and byways of inorganic chemistry, we now arrive at a different class of industries. There is no need to go into any detail, but suffice it to say that their influence has been of momentous importance industrially, and in turn has acted and reacted greatly on science. Merely to mention them is sufficient. I refer, of course, to dyestuffs and synthetic organic products, including drugs.[1] I will not weary you by repeating what has been related so often and so fully. It is, however,

[1] Among synthetic drugs there figures now the famous indicator phenolphthalein. Being colorless and tasteless itself while turning pink on the addition of soda, it has been added by Government to earmark certain kinds of hock. The quite unexpected result is that the indicator is now sold as a splendid aperient under the name of "Purgene."

noteworthy that from the outset, the establishment of new industries, based on the discovery of aniline dyes, and of methods of producing alizarin and indigo artificially, has in turn given rise to many others, as the organic and inorganic chemicals they required, which were little, if at all known to commerce at the time, had to be produced on a large scale. Benzol, nitrobenzol, aniline, to mention only a few, were among the newcomers, later on came anthracene.[1]

The coal tar industry is now the largest consumer of inorganic products and was the cause of the invention of the catalytic process of manufacturing sulphuric anhydride. May I be allowed to relate how I came to be connected with this industry? I was a pupil of Professor Strecker at Tübingen in the later sixties. When subsequently, in 187–, I again met him and his brother—who was a chemist at Hoechst—and Dr. Brüning, one of his pupils, he spoke of the importance of fuming sulphuric acid in the alizarin industry. The process of sulphonating anthraquinone had been introduced or was about to replace Perkin's dichloranthracene process, the use of ordinary concentrated oil of vitriol having proved to be very destructive to the anthraquinone at the elevated temperature that had to be employed. To my question how this fuming acid could best be made, he replied, "that is a problem for you to solve." A few experiments convinced me that, given pure gases, the catalytic action of platinum was the rational solution of the problem; I had to wait, however, for an opportunity of carrying my idea into practice. This came when, in April, 1875, a telegram reached me from my then principal, Mr. W. S. Squire, asking me to read up that night about Nordhausen acid as it was required by an alizarin works. I showed Squire how simple a matter it was to bring about the combination of sulphur dioxide and oxygen by means of platinum and other catalytics, but it was not until at his request I had carried out a number of experiments with bisulphates, etc., which were not very successful, that he asked me "to try my dodge;" henceforward we worked conjointly on the production of the anhydride by catalytic action. Though the process was patented in Squire's name, Sept., 1875, as others were afterwards or in the name of Neal (a clerk in a Patent Agent's office), they are the joint work of Squire and myself. Soon after, in the 2nd October Heft of *Dingler's Polytechnisches Journal*, Winkler published an account of his process which was practically identical with ours. Both of us erred at that time in believing that stoichiometrical proportions of the gases were the best to use, and the various similarities gave rise to unpleasant comment. In letters, however, which I possess, Winkler freely acknowledges the independence of our work and only regrets that he had deprived himself of the benefit of the invention of his publication, but he was anxious to work with us.

I cannot leave this chapter without paying my tribute to the work done by others in developing the catalytic process, and foremost, to the late Dr. Knietsch and his co-workers in the Badische Anilin- und Soda Fabrik. At the same time, I will let you into one or two secrets. The one is that so far I have not been successful in working with the spent oxide of gas works. It has the advantage of relative freedom from arsenic, but the drawback of producing an acid which is not so bright and colorless as that made from pyrites. The color is due to the organic matter in the raw material and to the formation of nitric oxide from its nitrogenous constituents. Nitric oxide can be traced in the burner gases and it is not eliminated in the washing process to which the gases are submitted. Another point is that there is a loss of platinum amounting to about 1 grain per ton of monohydrated acid produced; the loss must be of a mechanical nature and can be detected in the drips, although actinium is not discoverable in the gases at this enormous dilution. I believe I can find confirmation of the assumption that the platinum is carried forward owing to the rapidity of the current because in none of the processes I have worked at a relatively low velocity have I found any loss of platinum, except such as is unavoidable in extracting the asbestos.

Fuming sulphuric acid has found its chief use in the coal tar color industry, in refining certain petroleum oils—mainly the Russian oils—and vaseline, and in the explosive industry. As nitrocotton forms the basis of the celluloid industry, which has been so greatly developed of late, I must mention it and the rivals which it has found in acetyl and cuprammonium cellulose and last, but not least, in the viscose discovered by Cross and Bevan. These materials are used in large quantities for the production of artificial silk, photographic films and artificial hair; nor must I omit to mention the important wood pulp industries depending on chemical processes.

Sufficient examples have been given to illustrate my case: to show that science and industry are working hand in hand, and the importance of the result which such coöperation has produced.

In fact, no branch of industry has been left untouched by the ceaseless and irresistible advance of chemical science and technology.

And now when we look back on this long list of chemical industries which I have brought before you and their great variety, we have to ask ourselves: Can a chemist be so trained that on entering into any kind of works he will at once be of use and efficient, apart from the expectation that, as a matter of fact, he is supposed to be a proficient analyst? My answer is in the affirmative, provided that the employer himself knows something about the industry in which

[1] It is interesting to note that in the early days of aniline dyes, certain chemicals were smuggled in the works under a wrong name to hide their identity. I was at the time in the employ of Dr. Eugen Lucius, later a member of the firm Meister, Lucius und Co., hence this recollection. Great difficulties were experienced in recovering arsenic or disposing of the residues. A story is told with reference to these difficulties, amusing perhaps to all except those concerned in it. All troubles seemed to be over when some stranger appeared who undertook to dispose of these residues and was richly paid for his services. Ostensibly he had interested some capitalist in a "perfect process" for the recovery of the arsenic and had been advanced considerable sums for the alleged purchase of the residues which were warehoused as a security. As may be imagined, the *chevalier d'industrie* presently disappeared and the illegal storage and the strict regulations as to the disposal of arsenical material entailed a further considerable expenditure on the enterprising capitalist.

he is engaged; in that case, he will be patient and not expect too much from a beginner.

My illustrations must serve to show that if the student is but to know the chemical and physical principles which underlie so wide a range of activity as any one of the industries I have pictured provides, his time will be more than occupied; to expect him to be conversant also with the technical and economical aspect of industrial problems and to be able to apply his knowledge forthwith is going too far. Technical training can be of real value only after a sound foundation in the principles and practice of pure science has been acquired. Again do I ask: Can such technical knowledge be acquired by the student before entering into practice as well as the scientific knowledge that will be of use to him and his employers in all or the majority of the industries I have enumerated? It is evident it cannot; and if it cannot be done, is it worth the student's while to sacrifice much time at the most important and critical part in his life, as far as learning is concerned, in acquiring technical knowledge which may be of no assistance to him in after life?[1]

Too early concentration on special subjects must have a bad effect on the development of the power and habit of thinking independently and on the development of the faculty of imagination in the student. If he can find time, apart from his bread and butter education, it is much better for him to turn his mind to subjects of general culture, such as history, art and literature. Experience teaches me that technique is very readily acquired in practice by one who has been scientifically trained. The most important task of the employer in industry, as in every other walk in life, is to find the right man; and the right man with scientific knowledge, who has imagination and power of observation and can select and command competent subordinates, is immeasurably more useful than the otherwise right man without scientific knowledge. Before all things, it is necessary to find the right man; experience and inventive faculty must do the rest. It is not that we do not possess sufficient knowledge when we leave our college as students; what we lack is experience and the power of applying our knowledge. Our great chemical industries have been originated and developed by scientifically trained men; to name only a few, men such as Perkin, Caro, Brunck, Solvay and Mond, Young, the Siemens's, Duisburg, have never found any difficulty in securing the coöperation of engineers or electricians competent to construct any kind of plant they have required to carry out their problems.

In fine, Carlyle has well said: "He who has learned how to learn can learn anything;" the best system of education is the system which teaches each man how to educate himself.

Our education really begins when we leave college and the storm of life forms our character. We have to study, as nothing in this world is given to us for nothing; books, our scientific and technical societies,[1] must assist us.

Had time permitted, much might have been said of industries which are almost specifically American and of developments that are now taking place in connection with the manufacture of food supplies. My difficulty has been merely to indicate the vast number of directions in which the chemist is now rendering service to Society. Each one of my hearers will be able to enlarge upon one or the other of the topics to which I have referred. I can ask you now only to reflect how much lies behind my story. The progress witnessed in my time is inconceivable. It is impossible for one of my position to do justice to such a theme, but of its infinite importance to our civilization there can be no question.

[1] To a father's request to lay stress on his son obtaining particular knowledge about his own (the father's) industry, one of my professors replied: "You do not teach your son gymnastics in order that he shall be efficient when a man is turning somersaults in competition with others."

OXIDATION OF ATMOSPHERIC NITROGEN AND DEVELOPMENT OF RESULTING INDUSTRIES IN NORWAY.[2]

By Samuel Eyde.

We all know that the atmosphere surrounding us is composed of nitrogen and oxygen; to create by the union of these two elements new chemical combinations that can be utilized in the world's household is the task of the new industry.

(The work of Priestley and Cavendish, Crookes and Rayleigh and Ramsay, and Lovejoy and Bradley along this line was mentioned briefly but with appreciation.) The difference between previous methods and that of Birkeland-Eyde is that the latter have applied large quantities of electric energy in the electric arc, and have first found out the best method of doing this, while it was previously believed that it was small quantities of energy that gave relatively the best results. It is on that assumption that the apparatus employed by them was constructed.

In the Birkeland-Eyde method, the electric flames used in the electric furnaces start between the points of the electrodes which are close to each other. By this an easily movable and flexible current is established, which, with the arrangements made, will be found in a highly magnetic field. The electric arc that has been formed moves on account of this magnetic field with great velocity perpendicularly to the lines of force, and the electric arc's foot draws back

[1] These societies, the intercourse with professional friends engaged in the same pursuit as ourselves or in kindred industries, are invaluable to our education and so are their papers and periodicals. Unfortunately, most of us have to keep not one but quite a number of scientific periodicals and here we are faced with the fact that they all contain abstracts and that the same matter is abstracted in most of them, yet we cannot find this out till we have waded through them. Professor Noyes made an attempt to prevent this overlapping about ten years ago and the International Association of Chemical Societies, which held its first meeting in Paris in 1910 and met again in Berlin this year, will consider this problem among others in London in 1913. In the case of purely scientific chemistry, there should not be much difficulty in succeeding; as regards applied chemistry, objections have been raised, which our Council is now considering. Were it possible to rid ourselves of the incubus of overlapping abstracts, it would doubtless be a great saving of time to all of us and its realization should not be lightly set aside.

[2] Abstract of lecture delivered by Dr. Samuel Eyde, of Christiania, Norway, at a joint meeting of the Sections on Inorganic Chemistry, Physical Chemistry, Electrochemistry and Agricultural Chemistry at the Auditorium of the American Museum of Natural History. Eighth International Congress, New York, September, 1912.

from the points of the electrodes. When the length of the electric arc increases, the electric resistance becomes greater and the tension increases until it becomes so great that the new electric arc starts from the points of the electrodes.

To regulate the current, an inductive resistance is used in series with the flame. With alternating current all the arcs are formed alternating in opposite directions and appear to the eye to be circular discs. This flame is a powerful technical means for the oxidation of the nitrogen of the air. The flame in our furnaces burns with a steadiness that is really astonishing.

The electrodes are thick copper tubing, through which water passes for cooling them. The chamber in which the flame burns is circular, of only a few centimeters width, and about three meters diameter.

The interior of the furnaces is lined with fire clay brick, through the walls of which the air is admitted to the flame. The nitrous gases formed in the flame escape through a channel made along the casing of the furnace, which, like the flame chamber, is furnished with fire-proof bricks.

Each furnace is furnished with an induction coil, by means of which the power is regulated as required. The induction coil serves to make the flame in the furnace steady even while working. This furnace burns for weeks without any regulation worth mentioning. The maintenance of the furnace and its repair are simple, as the most exposed portions, the electrodes, require change only every third or fourth week, and then only a small part of them, and the fire-proof masonry every fourth to sixth month.

The temperature in our flames exceeds 3,000° C. The temperature of the escaping gases may vary between 800°–1,000° C. The furnaces are made of cast steel and iron, the middle of the furnace being built out to a circular flame chamber. The electrodes are led radically into this flame chamber. By aid of centrifugal fans the air is brought into each furnace through tubes from the basement.

From furnaces no longer than could be held in the hand, and which took an energy of some few horsepower we have attained two types which can, as mentioned, take an energy of more than 5,000 H. P. We have had in the course of this period of developing our method four experimental stations.

Some years later than the invention of our furnace, Dr. Schoenherr, with the electrician, Hessberger, of the Badische Company, perfected an electric furnace for the oxidation of the atmospheric nitrogen, which is built on quite a different principle.

In place of the great disc of electric flame he develops a long slender arc in the axis of a narrow iron tube, through which a current of air is forced.

The type now used consists of a somewhat slender vertical column of iron plates seven meters in height. The inner tube is the reaction chamber; the others form channels for the entrance of the air current and its exit after coming in contact with the flame. In this way the heat of the outgoing gas is transferred to the ingoing current.

At the lower end is the main electrode, movable in a vertical direction. The reaction tube serves as the second electrode. By means of a lever the space between the electrode and the tube can be bridged over and the arc formed. The air current, forced by a powerful aspirator, enters in the lower part of the furnace and passes the channels. The entrance to the reaction chamber is through a number of small tangential openings arranged in several horizontal rows in the sides. The current passes in this way from the chamber and the arc is driven up in the midst of the rapidly moving current of the air.

As a quick cooling is of importance in securing a good yield, the upper third of the tube has a water-jacket through which the gases pass, and in this way the reverse reaction is prevented to a notable degree.

The reaction is identical with that obtained in the Birkeland-Eyde furnace, and the yield, as far as the results now obtained show, is practically the same.

At Notodden we have only furnaces of the Birkeland-Eyde system, from 1,000 to 3,000 kw.

At Rjukan there are, however, furnaces of the B.-E. system, 3,000 kw., as well as furnaces of the Schoenherr system, all of 1,000 kw.

When the air in the flame chamber has been treated by the electric flames the nitrous gases formed pass out through pipes which convey the gas to the steam boilers, in which the temperature, which was, as mentioned, 1,000° C., is reduced.

The steam produced in the boilers is utilized in the further treatment of the products. In the boiler house there are also air compressors which supply compressed air for pumping acid and lye in the factory's various chemical departments. The gases pass on from the steam boilers through an iron pipe into the cooling house. Each cooler consists of a great number of aluminum tubes over which cold water runs, while the hot gases pass through them and are considerably cooled. From the cooling chambers the gases go on to the oxidation tanks.

These oxidation tanks are vertical iron cylinders lined with acid-proof stone. The object is to give the cooled gases a sufficient period of repose in which the oxidation of the oxide of nitrogen may take place. The necessary amount of oxygen is present in ample quantity in the air which accompanies the gases from the furnaces. From the oxidation tanks, the gases, by blast engines, are led into the absorption towers. All the towers are filled with broken quartz, which is neither affected by nitrous gases nor by nitric acid. To assist the passage of the gases, there are centrifugal fans constructed of aluminum on each row of towers. The gases enter at the base of the first tower, pass up through the quartz packing, and by a large earthenware pipe into the top of another tower, then downward through the quartz to the bottom of the second tower, and so on until the air, relieved of all nitrous gases, leaves the last tower. Water trickles through the granite towers, and this is gradually converted into a weak nitric acid, while the liquid used in the iron towers is a solution of soda. The absorbing liquid

enters the top of the tower and is distributed in jets by a series of earthenware pipes, so that the permeating gases come in immediate contact with the absorbing liquid. In the granite towers nitric acid is thus formed, and in the iron towers a solution of nitrite of soda.

The liquid emerges in a constant, even stream from the bottom of the towers, that from the granite towers running into the granite cistern. Hence it flows into the "montejus" which serve to pump up the acid, which has to pass repeatedly through the tower before it has become strong enough for the purpose for which it is intended. The "montejus" are worked by compressed air, and send the acid up into large stoneware tanks. From these jars the acid again runs through the towers as described. The "montejus" work automatically.

The iron towers are percolated, as already mentioned, by a solution of soda; otherwise the whole process is practically similar to that in the granite towers. The solution of soda, owing to its far greater power of absorption, effects the separation of the last remains of nitrogenous gases from the accompanying air. Of the entire quantity of nitrous gases passed through the absorption system about 97 per cent. is absorbed. The finished nitric acid from the towers, which has a strength of about 30 per cent. by volume, is collected in granite cisterns, from which it is drawn to what is called the "dissolution works." These consist of granite vats filled with limestone, over which the acid is poured. This drives off with violent effervescence, the carbonic acid contained in the limestone, while the nitric acid takes its place and forms a watery solution of nitrate of lime or calcium nitrate. The rest of the acid is neutralized in small towers filled with milk of lime, and is now pumped into vacuum evaporating apparatus. The object of boiling in vacuum is the great saving in the heat required.

The steam required for the evaporation is obtained from the steam boilers, heated, as before mentioned, by the furnace gases. The concentration of the nitrate solution in the evaporizing plant is continued until the specific weight of the liquid at an even temperature shows a content of 13 per cent. of nitrogen. This solution is then sufficiently evaporated and can be pumped up into the solidification chambers, where it is conducted upon a revolving cylinder, cooled on the inside, where it stiffens so quickly that it springs off in small leaf-like pieces, which can be granulated in the crushing mill. The coarse powder so produced is raised by an elevator to a vat, from the bottom of which it is tapped into casks holding 100 kilos net weight.

The gas led into the iron tower forms with the solution of caustic soda a solution of nearly pure sodium nitrite. This is concentrated by evaporation in the same sort of apparatus as above, and is allowed to crystallize. The crystals are dried in a centrifuge and tapped into casks.

The barrels are made at our own cooper's shop and are lined with paper to guard against the damp.

Besides these two products, nitrate of lime and nitrite of soda, we have during the last years at our Notodden Works taken up the manufacture of concentrated nitric acid and of nitrate of ammonia, which products have already won a good reputation, and in comparatively large quantities are shipped to the U. S. A. and other countries.

We are, however, in our industry not confined to these products hitherto mentioned. We have possibilities for the development of a whole series of new industries.

Visitors to our factories are often under the impression that the works are not running at all. There is but little noise and hardly any workmen are visible. Indeed it is remarkable how few people are required to run the establishments in our industry. Comparatively large working forces are needed only in the packing and wrapping departments.

For the development of the atmospheric nitrogen industry the question of water power is a vital one. Our industry cannot exist unless it can procure for itself cheap water power. There is hardly a country in the entire world that can boast of more favorable conditions in this respect than Norway, and the enormous rise of our industry must be attributed to a very large extent just to Norway's magnificent opportunities regarding the supply of the factories with water power. It must be borne in mind that Norway has not only her magnificent and high waterfalls, but that she has big lakes likewise in her mountains, allowing the construction of enormous natural reservoirs for leading the water to the power stations. Especially in the districts of our industry we enjoy most favorable conditions in this respect. The works now built are all situated in the southeastern part of Norway, in the Telemark River district.

The first works, the Notodden Nitrate Factories, are admirably situated at the lake of Hiterdal, about fifty feet above the level. A short channel with a series of locks permits communication with the town of Skien, an important seaport at the head of the fjord. Under the present conditions vessels of 100 tons burden can ascend to Notodden. It is planned to enlarge the locks so as to allow the passage of seagoing vessels of 2,000 tons.

The Notodden factories, which now have about 60,000 H. P. working, get this power from two neighboring waterfalls, Lienfos and Svaelgfos. At Lienfos, about two miles from Notodden, a dam with a fall of about fifty-five feet was completed in 1911. The volume of water is seventy-five cubic meters per second. The power station is equipped with four units, each of 5,000 H. P.

The Svaelgfos power house is situated above, about one mile from Lienfos. The volume of water is the same as at Lienfos. The dam secures, however, a fall of about 165 feet. A tunnel takes the water to the reservoir, from which four flumes cut in the solid rock conduct the water to the station where there are four sets of turbine generators, each of 10,000 H. P. The generators are capable of evolving 13,000 H. P., and rank among the largest units in the world.

The power of these two waterfalls is transmitted to Notodden by six separate lines. Each line con-

sists of six cables twelve millimeters in diameter. The three-phase alternating current of fifty periods is transmitted with a voltage of 10,000.

A second power station at Svaelgfos is now under construction. As the normal volume of water by an additional regulation of distant lakes in the same watershed soon will increase to ninety cubic meters, in the new power station likewise two additional units of 10,000 H. P. each are built.

About sixteen miles farther up the river the first regulating dam at the Lake of Tinn was constructed at the same time as the water station of Svaelgfos and the factories at Notodden. The immense basin regulated by this dam makes it possible to store up fully 300,000,000 cubic meters of water.

For the regulation of the water supply a dam was built at the Lake Mosvand by means of which the level of the lake is raised over 46 feet. As the surface of the lake is not less than 23 square miles, nearly 900,000,000 cubic meters can be retained. The minimum flow in the river is in this way increased from 5–47 cubic meters per second, or the water power at Rjukan only from 30,000 to 250,000 H. P.

To give you some idea of the development of our industry I let pass in review the factories we have had at the different times:

Dates.	Factories.	H. P. utilized.	Employees.	Workmen.
July 1903	Frognerkilens Fabrik	25	2	2
Oct. 1903	Anterlokken	150	4	10
Sept. 1904	Vasmoen and Arendal	1,000	6	20
May 1905	Notodden	2,500	4	35
May 1907	Notodden and Svaelgfos	42,500	12	103
Nov. 1911	Notodden, Svaelgfos, Lienfos and Rjukan I	200,000	143	1,340

According to the results of the use of our nitrate of lime, it is stated that it is the same as the Chile saltpeter and for certain soils it is even better. I have the pleasure of telling you that we to-day are sending many thousands of tons of the Norgersalpeter to California and Hawaii to be applied to the fruit orchards and sugar plantations; and the demand is twice as large as last year.

That our nitric acid and nitrate of ammonia are enjoying a good reputation is shown by the following extract from an English periodical, "*The Sphere.*" It was a peculiar coincidence that just on my trip over here I happened to see this paper and the article in question. There it reads—"Nitric acid is the main constituent of guncotton, dynamite and smokeless powders. One of the chemicals made at Notodden greatly reduces the heat of discharge, thereby prolonging the life of a big gun," and further: "Nitrate of ammonia obtained at Notodden by the marvelous electric process described here, is the principal constituent of many of the explosives for mines and is, therefore, of high importance to the navy." I could not wish anything better to be said in favor of our products; you would believe I had put it into the newspaper myself.

If you ask me what above all has contributed to such a rapid development of our industry, then I wish to mention the confidence the financial people gave and the good collaboration between engineers and myself. We all were filled with the same thought, to create something great and useful for our country, and we all had in view the great importance this new industry would have from an international point of view.

There is, however, one thing which I wish to tell you and which more than anything else has contributed to the great success attained in the development of this industry, and that is that I mainly have employed young men for this work. This assertion may appear strange but, I assure you that it is the "lack" of experience which has created this industry. If I had paid attention to all the doubt and hesitation brought forward by the so-called authorities during the development of our enterprise, the Norwegian people to-day would never have their nitrate industry. Thanks to the young people, to their undaunted courage, energy and love of action the work has been done, and it is in grateful remembrance of all our struggles in joy and sorrow, that I look backward to the work that has been done and the good results we have obtained to-day. The Norwegian nitrate industry is not alone a technical but also a financial success, and I have been able to keep my promise to the big financial institutions, the Banque de Paris and the Société Genérale, and also to our German associates, who to-day all are proud of the assistance and confidence they gave to the industry.

My own country, the small Norway, who is the youngest daughter of the family of the electrical industries, does no more need to be proud alone of the discovery of the South Pole, but is glad to be able to contribute her share in the solution of the most important questions relating to the world's household.

CURRENT INDUSTRIAL NEWS

By W. A. Hamor.

A NEW WOOD PRESERVATIVE.

"Aczol" is a new wood-preserving material, consisting of metallic ammoniates and an antiseptic acid. It is said to exert no harmful action on either wood or metal. Evidently the use of "Aczol" is based upon the process of permanently fixing large quantities of metallic salts in the wood, as in the patented process of Gerlache, wherein wood is impregnated with an aqueous solution containing free ammonia and ammonia compounds of copper and zinc (*e. g.*, ammoniacal solutions of copper sulphate and zinc chloride).

AIR COMPRESSOR LUBRICATION.

It is noted in *The Engineering and Mining Journal* (**93**, No. 23, 1125) that explosions within the cylinders of an air compressor are usually caused by the ignition of inflammable gas arising from the use of too much lubricating oil of low flash-point;

it is further pointed out that excessive use of oil tends to give rise to sticking of the valves. Attention is called to a lubricant which is free from these objections, namely, soapy water with which a small amount of flake graphite has been mixed. The graphite flakes remain suspended in the water until admitted to the interior of the cylinder, where they exhibit a tendency to attach themselves to the metallic surfaces, imparting a superficial glaze which is smooth, acquires a high polish and prevents actual contact of metal with metal. The soapy water may, however, cause rusting, so it is advisable to introduce a little oil into the cylinder when shutting down the compressor.

THE OXYGRAPH.

The oxygraph, described in *The Engineering Record* (65, No. 25, 701), is the latest appliance developed in connection with the oxy-acetylene-cutting process. It is constructed along the lines of the pantograph, the novel feature being a mechanically propelled tracer which gives uniform speed. The geared tracer is driven by an electric motor attached to the head of the machine. The oxygraph is said to cut steel 3 in. thick or less, at a speed of 6 in. per minute, and to be capable of cutting curves and right-angled corners. With high quality oxygen, the kerf is very narrow, and the cuts clean and sharp. The work is performed by guiding the tracer along the lines of the drawing on the tracer table, the torch cutting a reproduction in the steel ½ the size of the drawing. The appliance is said to be useful in die-making and for getting out difficult forms, as blanks for crank shafts of moderate dimensions.

THE MANUFACTURE OF LITHOPONE.

Lemaire states (*Sci. Am. Suppl.*, 74, 147) that the manufacture of lithopone is almost confined, in Europe, to Germany. A good deal of secrecy is observed in the manufacture—a fact which seems strange in view of the simplicity of the chemistry involved, but which is justified by the necessity of employing special machines in order to assure the cheapness and uniform quality of the product.

The quality of the lithopone depends largely upon the care exercised in the preparation of the two soluble salts, barium sulphide and zinc sulphate. These salts therefore are always prepared in the lithopone factory. Some German firms make a lithopone of the best quality, containing a large proportion of zinc sulphide, from which they obtain lower grades by admixtures of pulverized natural barium sulphate (heavy-spar), which is very cheap, but which absorbs oil far less perfectly than the precipitated barium sulphate which is contained in genuine lithopone.

The soluble barium sulphide is obtained by reducing heavy-spar (natural barium sulphate) by charcoal at a red heat, and

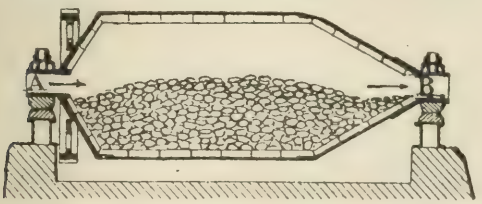

FIG. 1.—HARDINGE TUBE MILL.

leaching the mass after cooling with water. The heavy-spar and charcoal, according to Nagel, should be ground and mixed together in revolving tube mills, which can be cheaply operated. In the United States, the Hardinge tube mill (Fig. 1) is coming into use. The heavy-spar and charcoal are introduced at the end A and the pulverized mixture passes out at the opposite end B. Although the apparatus contains no sieve, the conical form of the vessel and its rotary movement produce an automatic gradation, so that only a finely ground mixture escapes at B, while the coarser particles remain in the mill for additional grinding. The reduction is accomplished in reverberatory furnaces, retorts or muffles. The operation may be either intermittent or continuous. In the latter case, the usual one when a reverberatory furnace is used, the mixture is deposited near the front of the furnace and pushed back at regular intervals. Continuously operating groups of vertical retorts (Fig. 2) or intermittently operating muffle ovens (Fig. 3) are also employed.

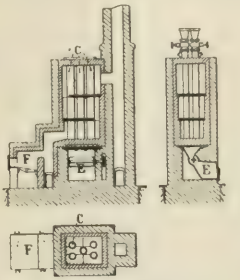

FIG. 2.—VERTICAL RETORTS: *C*, RETORTS; *E*, EXTRACTOR; *F*, FURNACE.

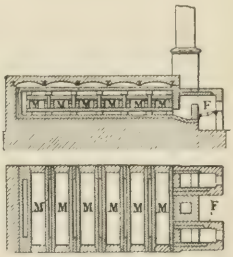

FIG. 3.—MUFFLE OVENS: *M*, MUFFLER; *F*, FURNACE.

In both of these cases the losses which are occasioned by oxidation in the reverberatory furnace are avoided, but the consumption of fuel is greatly increased.

In the United States, a revolving furnace like the Bruckner apparatus used in soda factories is employed. This furnace gives very good results, but its continuous rotation produces and disseminates dust, which must be removed by a collecting chamber placed between the furnace and the chimney. A furnace of this kind, 6 feet in diameter, 13 feet long, and making one complete revolution in two minutes, suffices for the production of 10 tons of lithopone per day. Nagel suggests the employment of the revolving furnace which is used for producing cement clinker, and which operates continuously and consumes little fuel.

The hot reduced mass is placed in iron cars, provided with sheet-iron covers, in order to prevent oxidation of the barium sulphide to sulphate, and allowed to cool. The leaching is

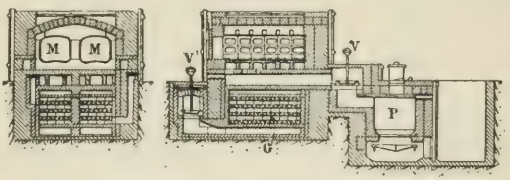

FIG. 4.—GAS-HEATED MUFFLE OVENS: *G*, RECUPERATOR; *M*, MUFFLER, *P*, GAS GENERATOR; *V*, GAS VALVE; *V'*, AIR VALVE.

accomplished in double-bottomed vats or in the Shank apparatus employed for the leaching of crude soda in the Leblanc process. The operation must be conducted rapidly in order to prevent oxidation.

All that part of the factory which is devoted to the preparation of barium sulphide should be separate and distant from the rooms in which the manufacture of lithopone takes place, for the smallest trace of charcoal dust or natural barium sulphate would destroy the whiteness of the lithopone. Natural barium sulphate is often very impure and frequently contains salts of iron and other metals. A trace of iron salt in the barium sulphide makes the lithopone sensitive to the action of light. Such traces of impurity are removed by methods which have been kept secret.

In Germany the zinc sulphate employed is obtained from

complex ores rich in zinc blende (natural zinc sulphide). These ores are roasted until the blende is converted into oxide and are then treated with sulphuric acid. In the United States, zinc white of inferior quality and natural oxides of zinc are sometimes used. It is also possible to employ zinc scraps dissolved in sulphuric acid. The crude solution of zinc sulphate is placed in a vat and mixed with granulated zinc or zinc scraps, which precipitate any copper and lead which may be present. The clear liquid is decanted and boiled with an admixture of chloride of lime, which oxidizes and precipitates the salts of iron and manganese as insoluble oxides. The mass is passed through a filter press and the clear liquid is collected in reservoirs.

In order to produce lithopone the solutions of zinc sulphate and barium sulphide are mixed in the desired proportions in a precipitating vat. The mixture is heated by steam for some time and the precipitate formed is separated in a filter press and washed with water. The drying is effected continuously in drying tunnels provided with blowers and heated by steam. The precipitate is placed in layers on wooden shelves in cars, which are drawn through the tunnel.

The dry product is heated to a dull red in muffles. The ovens are heated with charcoal or now, preferably, by recuperating gas generators (Fig. 4). The hot hard mass resulting is quenched in cold water, which causes it to crumble. It is again filtered out and dried, and is then pulverized and sifted. In general the final grinding is applied to the moist product before the final drying, unless it is possible to employ dry grinding in a tube mill of the Hardinge type.

THE POLLUTION OF STREAMS BY SPENT GAS LIQUOR.

H. M. M. Wilson (Industrial Hygiene Section, Royal Sanitary Institute, York, July 31, 1912) states that hitherto the large quantities of gas liquor produced in the manufacture of gas in England were regarded entirely as trade refuse, but are now considered of value, as considerable profit is derived from the recovery of ammonia from the liquor. The ever-increasing production of gas liquor is not dependent upon the manufacture of gas for illuminating purposes, but is also due to improved methods of coke manufacture and to the increased manufacture of power gas. Gas liquor contains ammonia in a free state and in combination with acids; this is recovered by distillation in two stages: by means of live steam and afterwards with the addition of lime. The hot vapors which pass from the still through sulphuric acid are cooled and condensed in a series of pipes into a grossly polluting liquid ("devil water"). This liquor is sometimes discharged as refuse, but is generally returned to the storage tank for gas liquors and is circulated again through the still. The bulk of the refuse comes from the still, being spent gas liquor after the ammonia has been expelled, along with lime added during the process. The spent gas liquor leaving the ammonia stills is a light brown liquid, of a temperature of some 100° C., turbid from particles of spent lime and tarry matters, and having a peculiarly offensive odor; it is strongly alkaline and exceedingly hard. The effect of a discharge like this upon a small stream is disastrous, the water being rendered poisonous, offensive, discolored, and unfit for ordinary use. Moreover, the great capacity of the refuse for absorbing oxygen is very detrimental to the stream in preventing self-purification. The purification of this kind of refuse has been a problem difficult to solve. It is easy to eliminate suspended solids by means of settling tanks; but these, though objectionable, are innocuous compared with the matters in solution. When diluted, the liquid is amenable to treatment on biological filters. Fowler has constructed a percolating filter of somewhat coarse material, 9 feet deep, and prepared it either by using material which had previously formed part of a sewage filter or by ripening the filter by the application of a weak sewage until nitrification was induced. To such a filter he has applied spent liquor from gas works clarified by settlement and diluted to 10 times its original volume either with clean water or with filter effluent at the rate of 100 gallons of the diluted liquor per square yard per day. This treatment effects a marked reduction in the oxygen absorbed figure, and sulphocyanides and phenols are also greatly reduced. However, the cost of carrying out the Fowler process is considerable, 2 to 3 cubic yards of filtering material being required for every 10 gallons of the crude refuse produced daily. For a battery of 40 coke ovens yielding 20,000 gallons of spent liquor daily, nearly ½ acre of filter 6 to 9 feet deep would be required; even after this purification, the liquor would still deleteriously affect a pure stream of small volume. It could, however, be used for many colliery purposes, *e. g.*, coke quenching and coal washing. Two methods of partial purification of spent liquor have been introduced by J. Radcliffe, who claims that all solids in suspension, all free lime, all hydrocyanic acid, 70 per cent. of the sulphocyanides, and 60 per cent. of the solids in solution, can be removed, and that the oxygen absorbed figure can be reduced by 75 per cent. In some collieries, the spent gas liquor is discharged into old pit workings, while in others the refuse is disposed of by passing it into trenches on the top of the spoil bank. Direct evaporation of the refuse in specially constructed furnaces has also been adopted in several instances. The latest developments in coke-oven plants will reduce the volume and alter the character of the refuse, so that the problem will be made easier.

THE MELTING POINTS OF FIRE BRICKS.

Kanolt (*J. Wash. Acad. Sci.*, **2**, No. 14, 337) has determined the melting points of fire bricks, taking as the melting point the lowest temperature at which a small brick piece could be distinctly seen to flow. The experiments were conducted in an Arsem graphite resistance vacuum furnace, and the samples, which were from 1 to 2 cm. in diameter, were usually enclosed in a refractory tube to protect them from reducing gas and were heated at the rate of about 10° F. per minute when near the melting point. The temperatures were determined by means of a Morse optical pyrometer of the Holborn-Kurlbaum type.

It was found that in the case of certain bricks made of heterogeneous material of relatively low melting point, the melting points were slightly higher after six hours' heating to 1550°, apparently as the result of the gradual running together of dissimilar particles to form a mixture having a higher melting point than the most fusible of the original materials.

The results are summarized in the following table:

MELTING POINTS OF FIRE BRICKS.

Material.	Number of samples.	Melting point Centigrade.
Fire clay brick	41	1555–1725 mean 1649
Bauxite brick	8	1565–1785
Silica brick	3	1077–1705
Chromite brick	1	2050
Magnesia brick	1	2165
Kaolin	3	1735–1740
Bauxite	1	1820
Bauxite clay	1	1795
Chromite	1	2180
Pure alumina		2010
Pure silica		1750

The value 1750° given for silica is not the true melting point, but represents approximately the temperature at which the silica flows distinctly. It was found that silicon carbide does not melt below 2700°; it becomes unstable at much lower temperatures.

"PERSIL" AS A BLEACHING AGENT.

According to *Revue Sci.*, **13**, 407, sodium perborate, under the name of "Persil," is now used for bleaching linen. A solution of sodium perborate heated to 60° C. gives sodium metaborate and oxygenated water. For bleaching cotton, it is first boiled with

"alkasil" (sodium monosilicate), and then in a bath containing 5 per cent. of sodium perborate. The temperature should be below 25° C. for bleaching flax, hemp, jute, and ramie, in which cases hypochlorites, sodium peroxide and sodium perborate are used concurrently. Sodium perborate gives a decided white color after steeping several hours at 70° to 80° C. and maceration, and after the use of hypochlorites acts as an antichlor. Straw may be bleached by the use of sodium peroxide or perborate in a solution acidified with oxalic acid, and a 1 per cent. solution of sodium hydrosulphite ("blankit") is also employed. Wool is bleached by sodium perborate, preferably in water acidified with lactic acid; but to bleach silk it is first necessary to wash in soapy water mixed with benzine, to remove the fatty matters, and then to treat with a bath of 1,000 liters of water containing 10 kilograms of cocoanut-oil soap and 2 to 3 kilograms of sodium perborate.

THE DISINFECTION OF POTABLE WATERS BY CHLORIDE OF LIME.

At the Fifty-third General Convention of the German Union of Gas and Water-gas Manufacturers at München, on June 24–28, 1912, Professor Bruns gave an account of the disinfection of drinking water by means of chloride of lime. Twenty years ago Traube used chloride of lime for the disinfection of water. His experiments were confirmed by Kratschmer and others, but were contradicted by Engel, who claimed that it is impossible to kill all pathogenic bacteria completely. This process has not been employed in Germany, but has been used for a number of years in the United States for the purpose of disinfecting water. The employment of this method is dependent upon the cheapness of chloride of lime, which varies with its hypochlorite content, the average being from 35 to 38 per cent. The disinfecting action of chloride of lime was first determined by Robert Koch, who showed that chlorine is one of the strongest disinfecting agents, and his experiments were confirmed later. Bruns states that the "chlorine" is dissolved in 100 parts of water and allowed to flow into the main stream so that the relation becomes 1 : 500,000. The number of bacteria is greatly reduced, but the taste is impaired, although this is not generally complained of. With larger amounts of chlorine, the results were bacteriologically satisfactory, but complaints were received on account of the foreign taste. Bruns performed experiments wherein equal quantities of chloride of lime and calcium thiosulphate were used; the thiosulphate served to render the free chlorine in the water inactive. When sodium thiosulphate was used, many complaints were received on account of the bad taste of the water. Bruns considers that chloride of lime can not be used for every purpose, but is still valuable for purposes of sterilization; this process can not be used in the purification of dirty waters unless filtration is also resorted to. It should always be borne in mind that chloride of lime is a disinfectant and not a purifying agent.

AMMONIA EVAPORATION AND TRANSFORMATION IN SOILS.

The lower fertilizing efficiency of ammonium sulphate as compared with sodium nitrate has been ascribed to various reasons, including slowness of nitrification, fixation of nitrogen in organic forms, and evaporation of ammonia. Von Wlodeck (*Chem. World*, 1, 287) reports experiments on soils in sunken cylinders to determine the loss and transformation of ammonia from soils containing varying amounts of lime, silt, and clay. In the course of his experiments, varying applications of ammonium sulphate, either alone or in combination with superphosphate, were made. The loss of ammonia by evaporation, when the ammonium sulphate was used under conditions as nearly natural as possible, was very small. With a high lime content of the soil, and heavy application of ammonium sulphate, the loss was larger. There was little or no loss where a mixture of ammonium sulphate and superphosphate was used, and the deep application of the ammonium sulphate greatly reduced the loss. The results of the observations of von Wlodeck on the fixation of the ammonia in organic forms were not entirely conclusive, but indicated that the fixation in the case of a loam soil was practically the same whether ammonium sulphate was used alone or mixed with superphosphate. On a light soil, superphosphate seemed to increase nitrogen fixation, and the addition of superphosphate apparently did not effect nitrification.

THE LOCATION OF UNDERGROUND PIPES.

A device for indicating the positions of pipes in waterworks systems, in cases wherein repairs or new connections are to be made, is being manufactured by a Quincy, Ill., concern and is now being used by a number of water companies. It is based upon the principle of causing a slight flow of electric current in the pipe, which thereby becomes a conductor. When an electric coil is brought within the field of this conductor, a current will be induced in the coil and cause a sound in a telephone receiver connected to the coil. The sound increases or decreases as the coil is carried nearer to or farther from the underground conductor, but ceases when nearest to it, that is, when directly over it. The situation of the pipe is thus determined by locating a number of points directly over it. In making use of the instrument, wires from a portable battery are attached to suitable connections and the operator, carrying the instrument in his hand and the receiver at his ear, walks across the supposed line of the pipe, the exact position being indicated by the absence of sound. In locating a service pipe, the battery wires are connected to the house cock and hydrant, causing a current along the service line.

THE CASTING OF MAGNESIUM ALLOYS.

Owing to the affinity of magnesium for oxygen, difficulties arise in casting alloys containing this metal. According to U. S. Patent 1,028,216, of June 4, 1912, Hoffman and Suchy have found that this reaction is mitigated by the addition of a small amount of calcium to the alloy. It is claimed that alloys thus formed may be cast without the formation of either magnesium oxide or nitride, or any other injurious action occurring. For example, magnesium and its alloys, when mixed with from 0.1 per cent. to 0.5 per cent. of calcium, flow without the occurrence of burning or the formation of a dark skin on the surface of the metal. The castings, moreover, do not effloresce in air and fill the molds perfectly, and the property imparted by the calcium is not lost on repeated fusion and casting. The calcium may be applied in the form of calcium oxide or may be added during the electrolytic production of magnesium. No characteristics of a calcium alloy are imparted, as the calcium or calcium oxide is used in such small quantities.

NOTES AND CORRESPONDENCE

OBITUARY—FREDERICK J. MAYER.

Mr. Frederick J. Mayer was born at Bremerhaven, Germany, July 4, 1853. He received his early education at the University of Stuttgart, Germany, and came to this country in 1870 after the Franco-Prussian War, in which he saw active service. Being an engineer, he engaged with the Bartlett Hayward Company of Baltimore, Md., as draftsman and while with them, up to 1906 as Chief Engineer, he designed, erected and operated many of the

large gas plants constructed by that company. In 1906 Mr. Mayer severed his connection with the Bartlett Hayward Company and organized and established the Didier-March Company in the United States, taking the position of General Manager.

Having made a life study of the carbonization of coal for metallurgical and domestic purposes, to him must be credited the establishing of some of the best foreign apparatus in the United States for the carbonization of coal by both the intermittent and continuous system in vertical retorts for gas house practice. He not only secured these rights for the United States, but he promoted the companies, erected the plants and put them in successful operation.

Mr. Mayer had invented many improvements for the manufacture of illuminating gas, patents of which were secured in the United States, Germany, France and England.

At the time of his death Mr. Mayer was 59 years old, an ardent and tireless worker, well known in the United States and abroad; a member of the American Gas Institute, the American Society of Mechanical Engineers, the Illuminating Engineering Society, Chemists' Club, American Peat Society, German Club and many other social and technical organizations.

Mr. Mayer is survived by his widow.

JAS. V. V. COLWELL.

THIRD INTERNATIONAL RUBBER CONFERENCE.

The Third International Rubber Conference convened at the Grand Central Palace in New York City, September 24–30, 1912.

After a careful consideration of the subjects discussed at the International Congress of Applied Chemistry, it was considered desirable to take up at the Rubber Conference those topics which appeared to be of more immediate importance to the manufacturer and consumer. Specifications for Materials, especially fire hose, were considered in detail. Probably the first attempt which was made to bring rubber goods manufacturers in consultation with the consumer was the Navy Conference, which was held within the past year, and which brought out such a frank expression of opinion.

The Executive Committee, which was formed to act in an advisory capacity to the Conference, consisted of the following:

Henry C. Pearson, New York, *President;* Frederic Dannerth, Ph.D., *Honorary Secretary;* E. S. Land, U. S. N., Washington; D. A. Cutler, New York; Dr. Lothar Weber, Boston; Dr. W. C. Geer, Akron, Ohio; Dr. S. P. Sharples, Boston; Dr. Eugenio Dahne, Brazil; C. E. S. Baxendale, Federated Malay States; F. Crosbie-Roles, Ceylon; A. Staines Manders, London.

Fifteen of the principal American railways were represented at the Conference through their chief chemists and engineers of tests.

The following organizations and Governments were represented by official delegates:

American Chemical Society, American Society for Testing Materials, Society of Chemical Industry, American Institute of Chemical Engineers, German-American Technical Society, Institute of Operating Engineers, U. S. Department of the Navy, U. S. Department of Commerce and Labor, U. S. Department of the Interior, U. S. Isthmian Canal Commission, The Official Material Testing Bureaus of the principal foreign Governments, The Factory Mutual Laboratories of Boston, Mass., Federal Government of Brazil, Federated Malay States and Straits Settlements, Ceylon, Hawaiian Islands, Province of Moro, Philippine Islands, Burma (India), The State of Amazonas (Brazil), The State of Matto Grosso (Brazil), The State of Para (Brazil), The State of Acre (Brazil), The State of Minas Geraes (Brazil), Bolivia, Republic of Honduras, State of Bahia (Brazil).

SCHEDULE OF MEETINGS.

Tuesday, Sept. 24th, at 2 P.M.—An address of welcome by the President, Mr Henry C. Pearson. Topic discussed, "*Crude Rubber*." Special papers

"*Rubber Contracts,*" Arthur W. Stedman.

"*The Plantation Industry,*" Cyril E. S. Baxendale, Esq., of the Federated Malay States.

"*Various Manihots Producing Rubber in the Central States of Brazil,*" J. Santiago Cardwell Quinn, Commissioner.

"*Possible Rubber Producers in the Temperate Zone,*" Charles P. Fox, Akron.

"*Some Effects of Acclimatization upon Guayule. Parthenium Argentatum,*" Francis E. Lloyd, Montreal, Canada.

Wednesday, Sept. 25th, at 10 A.M.:

"*Problems in Vacuum Drying,*" J. P. Devine.

"*Manufacture of Dipped Goods,*" T. W. Miller.

"*Physical Methods of Testing Rubber and Rubber Products,*" P. L. Wormeley, Bureau of Standards, Washington.

"*Factory Management and Organization Methods,*" J. C. Jurgensen (President of the Institute of Operating Engineers), and Frederic Dannerth (Consulting Chemist).

Thursday, Sept. 26th, 10 A.M.:

"*A Brief History of Fire Hose Specifications,*" E. A. Barrier.

Topical discussion on specifications (mechanical rubber goods for railroads, Federal and Municipal Governments), including as sub-topics: Air brake hose, railroad steam hose, fire hose, navy packings, etc.

"*The Commercial Possibilities of Synthetic Rubber,*" L. E. Weber, Boston, Mass.

Friday, Sept. 27th, at 10 A.M.—A report of the transactions of the Navy Conference at Washington, December, 1911, E. S. Land, U. S. N. Topical discussion on specifications: (*a*) Materials for insulated wire; (*b*) Textile materials (sheeting, duck and yarns).

A preliminary report of activity by the "Railroad Committee" on "*Standard Methods of Testing Rubber Products.*"

At 7 P.M.—Informal dinner for rubber chemists and engineers.

Saturday, Sept. 28th, at 10 A.M.—Meeting for the presentation of resolutions and recommendation of official methods for physical testing and chemical analysis of crude gum and manufactured rubber goods.

MUNICIPAL WATER CONSERVATION EXHIBIT OF THE CITY OF PHILADELPHIA.

The Department of Public Works of the City of Philadelphia is to open on or about the seventh day of October this year, and continue for two weeks, a noteworthy exhibit pertaining to the use and waste of the municipal water supply. This exhibit will be held in the courtyard of City Hall and every endeavor will be made to make it of great educational value to the people.

Suitable booths will be erected so that all the interesting exhibits displayed at the time will be properly protected from any adverse weather conditions.

In addition to the official display of the Department of Public Works, all the local manufacturing and jobbing trade in water appliances have been invited to show every device and apparatus pertaining to the use, but particularly to the conservation of water.

It is the idea of the Department of Public Works to make this exhibit entirely along popular lines, easily understood by everyone and to so educate the consumer of water that the enormous waste which now obtains in this City may be reduced thereby to a minimum.

There will be much in this exhibit of interest to Engineers, and all those connected in any way with municipal water plants, architects, and students of civic affairs in general. All inquiries on the subject should be addressed to H. W. Benjamin, Room 790, City Hall, Philadelphia, Pa.

NEW PUBLICATIONS

By D. D. Berolzheimer, Librarian, Chemists' Club, New York.

PAPERS OF SPECIAL INTEREST TO INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS FROM THE PROCEEDINGS OF THE EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

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Alcohol; The Production of— and Sugar from the Sap of the Nipa Palm. By H. D. Gibbs. Vol. 8, pp. 13–19.

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Alkaline Salts; On Recent Progress in the Electrolysis of—. By M. Wilderman. Vol. 21, pp. 185–196.

Alloy; A New— with Acid Resisting Properties. By S. W. Parr. Vol. 2, pp. 209–213.

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Analysis; Cadmium Nitrate in Qualitative—. By Anton Vorisek. Vol. 17, pp. 91–102.

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MARKET REPORT.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF SEPTEMBER.

ORGANIC CHEMICALS.

Acetanilid	Lb.	$20\frac{1}{2}$	@	23
Acetone (drums)	Lb.	17	@	18
Alcohol, grain (188 proof)	Gal.	2.55	@	2.57
Alcohol, wood (95 per cent.)	Gal.	50	@	52
Alcohol, denatured (180 proof)	Gal.	40	@	42
Amyl Acetate	Gal.	2.75	@	2.95
Acetic Acid (28 per cent.)	C.	2.00	@	2.15
Aniline Oil	Lb.	$10\frac{3}{4}$	@	$11\frac{1}{2}$
Benzoic Acid	Lb.	23	@	27
Carbon Tetrachloride (drums)	Lb.	11	@	16
Carbon Bisulphide	Lb.	14	@	15
Chloroform	Lb.	20	@	30
Carbolic Acid (drums)	Lb.	14	@	15
Citric Acid (domestic), crystals	Lb.	$38\frac{1}{2}$	@	39
Camphor (refined in bulk)	Lb.	44	@	—
Dextrine (imported potato)	Lb.	6	@	7
Dextrine (corn)	C.	3.20	@	3.31
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	$8\frac{1}{2}$	@	$9\frac{1}{2}$
Glycerine (dynamite)	Lb.	$17\frac{3}{4}$	@	$18\frac{1}{4}$
Oxalic Acid	Lb.	$7\frac{7}{8}$	@	$8\frac{3}{8}$
Pyrogallic Acid (bulk)	Lb.	1.35	@	1.45
Salicylic Acid	Lb.	31	@	33
Starch (corn)	C.	2.45	@	2.56
Starch (potato)	Lb.	$5\frac{1}{4}$	@	$5\frac{3}{4}$
Tannic Acid (commercial)	Lb.	35	@	$35\frac{1}{2}$
Tartaric Acid crystals	Lb.	$30\frac{1}{2}$	@	31

INORGANIC CHEMICALS.

Acetate of Lime (gray)	C.	2.50	@	2.60
Acetate of Lead (brown, broken)	Lb.	$7\frac{3}{4}$	@	8
Alum (lump)	C.	1.75	@	2.00
Ammonium Carbonate, domestic	Lb.	8	@	$8\frac{1}{2}$
Ammonium Chloride, gray	Lb.	$6\frac{1}{8}$	@	$6\frac{1}{4}$
Aluminum Sulphate	C.	90	@	1.75
Aqua Ammonia (drums) 16°	Lb.	$2\frac{1}{4}$	@	$2\frac{1}{2}$
Arsenic, white	Lb.	$4\frac{3}{4}$	@	5
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Barium Chloride	C.	1.40	@	1.55
Barium Nitrate	Lb.	$4\frac{3}{4}$	@	5
Borax, crystals (bags)	Lb.	$3\frac{1}{2}$	@	4
Boric Acid, crystals (powd.)	Lb.	7	@	$7\frac{1}{2}$
Bromine, bulk	Lb.	25	@	30
Bleaching Powder (35 per cent.)	C.	1.25	@	1.45
Barytes (prime white, foreign)	Ton	18.50	@	22.50
Blue Vitriol	Lb.	$5\frac{1}{2}$	@	$5\frac{3}{4}$
Calcium Chloride	C.	65	@	90
Chalk (light precipitated)	Lb.	$4\frac{1}{2}$	@	6
China Clay (imported)	Ton	11.50	@	18.00
Feldspar	Ton	7.00	@	9.00
Fuller's Earth, powdered	C.	80	@	85
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1.15	@	1.55
Iodine (resublimed)	Lb.	3.05	@	3.10
Lead Nitrate	Lb.	$8\frac{3}{8}$	@	$8\frac{1}{2}$
Lithium Carbonate	Lb.	65	@	70
Magnesite (raw)	Ton	7.50	@	8.50
Nitric Acid, 36°	Lb.	$3\frac{7}{8}$	@	$4\frac{1}{4}$
Phosphorus	Lb.	35	@	90
Phosphoric Acid, sp. gr. 1.75	Lb.	22	@	26
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bromide	Lb.	31	@	34
Potassium Permanganate (bulk)	Lb.	$9\frac{3}{4}$	@	10
Potassium Cyanide (bulk) 98–99%	Lb.	19	@	24
Potassium Iodide (bulk)	Lb.	2.60	@	2.65
Potassium Chlorate, crystals	Lb.	$8\frac{1}{4}$	@	$9\frac{1}{2}$
Potassium Nitrate (crude)	Lb.	5	@	$5\frac{1}{8}$
Potassium Bichromate, 50°	Lb.	$6\frac{7}{8}$	@	7
Quicksilver, Flask		42.00	@	43.00
Salt Cake (glass-makers')	C.	55	@	65
Silver Nitrate	Oz.	$39\frac{7}{8}$	@	42
Soapstone in bags	Ton	10.00	@	12.00
Sodium Acetate	Lb.	$4\frac{1}{4}$	@	5
Sodium Chlorate	Lb.	$8\frac{1}{4}$	@	$9\frac{1}{2}$
Sodium Bicarbonate (English)	Lb.	$2\frac{3}{4}$	@	3
Sodium Bichromate	Lb.	$5\frac{1}{8}$	@	$5\frac{1}{4}$
Sodium Hydroxide, 60 per cent.	C.	1.60	@	1.65
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent., spot	C.	$2.52\frac{1}{2}$	@	—
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	$6\frac{7}{8}$	@	$7\frac{3}{8}$
Sulphur, Roll	C.	1.85	@	2.15
Sulphur, Flowers (sublimed)	C.	2.20	@	2.60
Sulphuric Acid, 60° B.	C.	85	@	1.00
Talc (American)	Ton	15.00	@	20.00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	$13\frac{1}{4}$	@	$13\frac{1}{2}$
Tin Oxide	Lb.	48	@	50
Zinc Chloride (granulated)	Lb.	$4\frac{1}{4}$	@	$4\frac{1}{2}$
Zinc Sulphate	Lb.	$2\frac{1}{4}$	@	$2\frac{1}{2}$

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	40	@	44
Black Mineral Oil, 29 gravity	Gal.	12	@	$12\frac{1}{2}$
Castor Oil (No. 3)	Lb.	$9\frac{1}{2}$	@	$10\frac{1}{2}$
Ceresin (yellow)	Lb.	9	@	15
Corn Oil	C.	6.10	@	6.15
Cottonseed Oil (crude), f. o. b. mill	Gal.	$37\frac{1}{4}$	@	38
Cylinder Oil (light, filtered)	Gal.	$19\frac{1}{2}$	@	20
Japan Wax	Lb.	$10\frac{1}{4}$	@	$10\frac{1}{2}$
Lard Oil (prime winter)	Gal.	87	@	92
Linseed Oil (double-boiled)	Gal.	70	@	72
Paraffine Oil (high viscosity)	Gal.	$25\frac{1}{2}$	@	26
Paraffine (crude 120 & 122 m. p.)	Lb.	$3\frac{1}{4}$	@	$3\frac{3}{4}$
Rosin Oil (first run)	Gal.	36	@	37
Spindle Oil, No. 1	Gal.	16	@	$16\frac{1}{2}$
Sperm Oil (bleached winter), 38°	Gal.	72	@	74
Stearic Acid (double-pressed)	Lb.	$9\frac{1}{4}$	@	10
Tallow (acidless)	Gal.	62	@	65
Tar Oil (distilled)	Gal.	30	@	31

METALS.

Aluminum (No. 1 ingots)	Lb.	$21\frac{1}{2}$	@	$22\frac{1}{2}$
Antimony (Hallet's)	Lb.	$7\frac{3}{4}$	@	$8\frac{1}{2}$
Bismuth (New York)	Lb.	2.10	@	2.15
Copper (electrolytic)	Lb.	17.35	@	$17\frac{1}{2}$
Copper (lake)	Lb.	$17\frac{5}{8}$	@	$17\frac{3}{4}$
Lead, N. Y.	Lb.	5.10		
Nickel	Lb.	50	@	55
Platinum (refined)	Oz.	46.35	@	47.00
Silver	Oz.	$63\frac{1}{4}$	@	—
Tin	Lb.	49.20	@	49.30
Zinc	Lb.	7	@	—

FERTILIZER MATERIALS.

Ammonium Sulphate	C.	3.30	@	—
Fish Scrap, domestic, dried	Unit	2.45	&	10
Blood, dried	Unit	2.75	@	—
Tankage, high grade	Unit	2.60	@	2.65 & 10
Bone, $4\frac{1}{2}$ and 50, ground, raw	Ton	28.00	@	—
Potassium, "muriate," basis 80%	Ton	38.55	@	—
Phosphate, acid, 16 per cent.	Ton	6.75	@	7.00
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.	Ton	3.70	@	3.80
Tennessee, 68–72 per cent.	Ton	4.25	@	4.50
Pyrites, furnace size, imported	Unit	$0.13\frac{1}{8}$	@	$0.13\frac{1}{4}$
Castor meal	Unit	nominal		
Mowrah meal	Ton	8.50	@	9.00

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume IV NOVEMBER, 1912 No. 11

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Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Penna., under the Act of March 3, 1879.

ESCHENBACH PRINTING COMPANY, EASTON, PENNA.

TABLE OF CONTENTS

EDITORIALS:
- Morris Loeb 784
- The Incongruities of American Patent Litigation 785

ORIGINAL PAPERS:
- Distillation of Resinous Wood by Saturated Steam By L. F. Hawley and R. C. Palmer 789
- The Determination of Oxygen in Iron and Steel by Reduction in an Electric Vacuum Furnace. By Wm. H. Walker and Walter A. Patrick 799
- The Methods of the United States Steel Corporation for the Commerical Sampling and Analysis of Pig Iron. By the Chemists' Committee of the U. S. Steel Corporation 801
- The Synthesis of Hydrocarbons at High Temperatures and Pressures. By J. N. Pring and D. M. Fairlie. 812
- Glass Formulas: A Criticism. By Alexander Silverman 818
- On the Density of Some Borate and Silicate Glasses. By Edwin Ward Tillotson, Jr. 820
- Extraction of Thoria. By Charles Baskerville 821
- The Production of Available Potash from the Natural Silicates. By Allerton S. Cushman and George W. Coggeshall 821
- Potash, Silica and Alumina from Feldspar. By Edward Hart 827
- Composition of the Salines of the United States. By J. W. Turrentine, with analyses by A. R. Merz and R. F. Gardner 828
- The Determination of Phosphorus in Commercial Acetylene. By L. M. Dennis and W. J. O'Brien ... 834
- The Determination of Lead Sulphate and the Ultimate Estimation of Sublimed White Lead in Rubber. By John A. Schaeffer 836
- The Effect of Kiln-Drying at 145° F. on the Composition of the Hop. By H. V. Tartar and B. Pilkington 839

LABORATORY AND PLANT:
- Combination of the Contact Process with the Ordinary Lead Chamber or Tower Systems; an Improvement in the Manufacture of Sulphuric Acid. By William Wilke 840
- A Simple Test for the Determination of Butter-fat in Butter. By James M. Doran 841
- Apparatus and Method for Sulphur Determination in Petroleum Illuminating and Lubricating Oils. By P. H. Conradson 842
- Carbon Dioxide Absorption Bottle. By W. A. Koenig. 844
- A New Alloy with Acid Resisting Properties. By S. W. Parr 844
- Modified Bunsen Valve. By Leslie Russell Milford 845
- A Simple Form of Laboratory Support. By T. Linsey Crossley 846

OBITUARIES:
- Morris Loeb 846

CURRENT INDUSTRIAL NEWS:
- Plumbism in New York City 849
- The Chemical Industries of France in 1911 849
- The Denaturation of Alcohol with Pyridine 850
- The Status of the Artificial Silk Industry 850
- Another Rubber Substitute 850
- The State of the Platinum Market 850
- Increasing the Resistance of Alloys to Chemical Action. 851
- The Purification of Boiler-feed Water 851
- The Alkali Industry in Great Britain during 1911 851
- Sulphur Dioxide from Iron Pyrites 852
- A Hydrogen-supply for Dirigible Balloons 852
- "Durobax" Glass 852
- "Triplex" Glass 852
- Imports and Exports of Chemicals 852
- Acid-resisting Alloys 852
- The Schoop Metallizing Process 853
- The State of the Antimony Market 853
- Porous Metals 853
- Peat Fuel for the Production of Power 853
- A New Water-jet Air-pump 854
- The Parkinson Patent Furnace 854
- Reinforced Galvanized Spiral Pipe 854
- A New Automatic Water-jet Air-pump 854
- The Use of Graphite in Boilers 855

NOTES AND CORRESPONDENCE:
- The Third International Rubber Exhibition 855
- The Underwriters' Laboratories Extraction Apparatus: A Note 856
- Bureau of Standards Analyzed Samples 856
- The Determination of Benzaldehyde, Maraschino Cherries and Maraschino Liqueur: A Correction 856
- Phenol-formaldehyde Condensation Products: A Correction 857

BOOK REVIEWS:
- Industrial Chemistry; Foods and Drugs; Die Analyse der seltenen Erden und der Erdsäuren; Researches in Cellulose; Methods of Organic Analysis 857

NEW PUBLICATIONS 859

RECENT INVENTIONS 860

MARKET REPORT 862

EDITORIALS

MORRIS LOEB.

"Cast forth thy Act, thy Word, into the ever-living, ever-working Universe; it is a seed-grain that cannot die; unnoticed to-day, it will be found flourishing as a banyan grove after a thousand years."—*Carlyle.*

Many sad happenings in this world are accepted with silent stoicism because we are, in some measure, prepared for them. There are others which strike like a thunderbolt from a clear sky. Such was the announcement of the death of Morris Loeb.

Not so many days ago, he was among us in all the intensity of his active life, eagerly busy with the success of the International Congress of Applied Chemistry; guiding us by his example, helping us by every means at his disposal, sacrificing his personal comfort, taking no rest even after the first symptoms of the illness which has carried him away made his work very difficult—ever striving not to neglect anything that might contribute to the interest or the enjoyment of the visitors to the Congress.

He passed away as he has lived: never minding himself when catering to the welfare and the comforts of others.

If I had to sum up the character of Morris Loeb, if I had to give the key to his whole life, I would call him the incarnation of the sentiment of duty and service.

Most men act by necessity; others by example; others again are animated by greed, by vanity, or other regrettable impulse. Whoever knew Morris Loeb intimately could perceive in every action, every thought, every effort, this sternly simple but sublime impulse of duty and service. Sometimes, his austerity in that direction went even to the point of disturbing his best friends, as well as heaping discomfort and sacrifice on himself.

I made his acquaintance some twenty years ago: met him regularly at our chemical meetings; then met him more intimately in the circle of his home life. The longer I knew him, the higher went my esteem, my affection for that unusual man, and the more his noble example stimulated me, as it has inspired so many others to better efforts.

I have had more than one lively discussion with him, where each of us was convinced of the strength of our own point of view; but in every instance did I leave him with greater respect and admiration. Those who saw him engaged in any action where he was combating with all the directness of his honest convictions, anything he believed was not for the best of purposes, had to know him intimately in order to grasp fully the intense underlying kindness, the consideration for the feelings of others, which he harbored in his big soul. An insincere or selfish thought never crossed his mind.

His way of doing good was different from the drowsy apathy or the contemplative attitude of some dreamy reformers; neither did he fret away his energies on ideals of the unattainable kind; his life was a life of action, of work—not of dreams, and his action was always measured with rare forethought towards a well defined purpose.

His parents, whose memory he worshiped, left him a large fortune; to their son this fortune appeared only as a large responsibility—as a power to do good—as a means to help other men to do more good.

His philanthropy was not of the kind which limits itself to signing a substantial check, or organizing a charity-festival, or other similar kinds of alm-charities which perpetuate poverty and misery and make the poor poorer and the weak more helpless. His philanthropic work went to the root of things: it meant the fulness of his own personal efforts with all the discomforts or self-abnegation this frequently implied. Then again, this same austere man could often unbend to the point of great joviality when his ever-ready wit saw a humorous point in a situation. I was never able to discover the slightest trace of vanity or conceit in him, and this made him invulnerable against scheming flatterers.

Dr. Baskerville has well described the scientist and the professor in his review of the career of our departed brother (p. 845). But what appeals to me as the greatest claim of gratitude from our profession, is the leading part Morris Loeb took in making the Chemists' Club building an accomplished fact by infusing his own idealism throughout the whole enterprise. Thus he has succeeded in making of the Chemists' Club an institution whose good influence is already reaching out near and far over the whole country; not only has it hastened the healthy development of our chemical organizations, but it is at the same time contributing to the growing importance and increased usefulness of the chemical profession to the community itself.

Whoever saw him at work in this instance, knows how he conceived and carried out practically every part of that project from the financial start to the successful operation thereof; how he attended, personally, to the most trifling details, when he thought that by doing so he might better insure the proper working of his carefully planned organization. Many a nook or corner of our Club house reminds us of his personal solicitude,—nay, of the very touch of his hands, where he helped to place a work of art or some other object of interest gathered purposely by him for the Club during his late travels.

The day of his death, October the eighth, was exactly the third anniversary of the date on which he signed the incorporation papers of the Chemists' Building Company.

Vividly do I remember the day when he first outlined to me the whole project: "It can be done," said he, "if we all work together. We can do it in such a dignified and direct way that nobody can claim that it is a one-man's affair or a gift. Neither should it be a cold-blooded business proposition, although

it ought to be carried out on business lines. I know already a few men who are willing to guarantee a substantial subscription, and who may help me to find others to help us along." With characteristic consideration, he added: "Above all, it should be well understood that he who is unable to help financially, can still be a great contributor to the success of the work, if he will aid us by any personal effort, even if it be only by his enthusiasm."

In this instance, as always, he never mentioned his own name, and tried for a while to shield his identity by referring to "his acquaintances" or "some friends of his." This was ever his favorite way of designating any financial help he intended to furnish himself.

Even after the meeting at Toch's residence, where Bogert, Baskerville, Toch and myself, were present, several did not yet fully realize that Morris Loeb was going to furnish the initial funds.

If, in this instance, he contributed freely with his money, he rendered much greater service by his continuous personal work for three full years, until he was convinced that everything was as it ought to be, and the Chemists' Club was safe and sure.

Wherever he was, he found some way of being of service or help towards others. I am told that when he went to study in Germany after graduating from Harvard, he there led the quiet, modest life of a hard-working student, and that of the allowance his rich father sent him, very little was used for his own personal comfort, but most of it found its way to help others who never knew who had assisted them. Whatever he did in the matter of money contributions, he carefully arranged everything so as to keep himself in the background, but his personal work was ever so much the more in evidence.

Another one of his traits was that great feeling of reverence and gratitude towards some of his former professors as well as to his Harvard Alma Mater; but whatever he did was done as if he were a mere incident in it; even his intimate friends, who did not belong to Harvard, learned only by accident how he and his brother had made a foundation in honor of his departed professor, Wolcott Gibbs. And when last year, he organized the Wolcott Gibbs' Memorial Day at the Chemists' Club, and presented the bust of Wolcott Gibbs on that occasion, he kept himself very much in the background, although attending painstakingly to every detail so as to make sure that nothing should mar the success of the event, which he had planned alone in his great love for his former teacher.

He abhorred any display of wealth or self-importance, and this made his company so much the more liked by his fellow chemists.

Those who knew his home life, will remember how he filled his days, alternating his devotion to his duties and philanthropies with acts of kindness and consideration to his family, and his friends: all this frequently interwoven with banter and wit.

Having no children, he and his distinguished wife gave an outlet to their natural feelings by furthering the comfort and happiness of the children of their friends and by assisting the unfortunate children of the poor or helpless.

Of some men, it can be said: The whole world is their country, humanity is their family, and to do good is their religion. Morris Loeb was one of such men.

Whatever there was to be done, one could count on him. Whether the matter was very important or not, once he had accepted to serve, he never disappointed. When he had accepted membership on some committee or another, he was punctual at the meetings, and only very urgent matters could keep him away. Whenever he participated in anything, he gave body and soul to it.

His frank speech, simple words, direct arguments never strove for rhetorical effect, but aimed only at convincing others of his own earnest opinion. I still see him with his manly bearing, his handsome head, his deep-thinking, big, honest eyes, which flashed conviction and sincerity into every one of his arguments, and gathered respect from all who listened to him, whether they were of his opinion or not.

Noble friend, all who have known you enough have been made better by your example.

We shall miss much, yes very much, your inspiring personality.

Yet, the mention of your name will often serve to every one of us, as the guiding flash of a beacon, till we, too, shall reach the other shore.

L. H. Baekeland.

THE INCONGRUITIES OF AMERICAN PATENT LITIGATION.

Whoever was present at the White House Garden Party in honor of the members of the Eighth International Congress of Applied Chemistry must have been impressed by the directness of speech of President Taft.

One of our foreign visitors remarked to me: "Your President does not waste his time in pure formalities. Undaunted by his strained ankle and the hot weather, he left the comforts of Beverly to receive us here, and he gave us, at the same time, a refreshing sensation of the simple directness of your democratic government. Up till now, we were accustomed to the cut-and-dried speeches full of the usual meaningless platitudes with which royalty opened these Congresses. But the chief of your Republic gave us, in a few precise words, his opinion on what I consider one of the most important factors in the healthy industrial development of all civilized nations."

The speech of President Taft has been reported in full by This Journal (IV, 710). The following is the most striking part of it:

"Patents have played a very great part in the development of the United States, and we have given to patentees a very valuable monopoly for the purpose of discovering by their industries new methods of accomplishing useful results. Whether we have made this monopoly too great or not is the subject of consideration by a commission provided for by Congress.

"There is certainly great room for improvement in the machinery of our patent office, and it would be well if more value could inhere in the issuing of a patent as an evidence of real property. Now, however, until a patent has beeen fought through the courts, people do not seem to regard it as of a great deal of monopoly value.

"I may add that one of the great opportunities for reform, in my judgment, is in the shortening of patent litigation and the reducing of its expenditure. I know very little about chemistry, but I know a good deal about patent litigation. I know the amount of money that has been unnecessarily wasted and the inequality that has been produced between the rich litigant and the poor litigant by reason of the unnecessary expense of that litigation. This is one of the things that calls for an immediate remedy.

"It is not essential that we should make a record of 10,000 printed pages at $50 a day for experts and $100 a day for patent lawyers. I have no objection to experts. I have no objection to patent lawyers, but I think we can have too much of both of them."

Mr. Taft, as a former judge, has had ample opportunities to observe the delays, absurdities, and iniquities of patent litigation in this country. He has seen how patent suits degenerate into mere jockeying and in lawyers' acrobatics, and thus defeat the very purposes for which our patent system was created. In expressing his opinion in such non-equivocal terms, he put his finger on the sorest spot of our patent system. His statements are in direct accord with the views expressed so often by others. (*See Judge Hough's opinion in the Selden case; Baekeland, The Abuses of our Patent System*, THIS JOURNAL, *April, 1912; Editorial Metallurgical and Chemical Engineering, Vol. X, p. 387, July, 1912; Robert N. Kenyon, The United States Patent System, Transactions of the American Institute of Chemical Engineers, 1912, etc.*)

Whether Mr. Taft be reelected or not, it is of the utmost importance that his wise words should not be lost to the next administration upon whom, according to all appearances, will devolve the long deferred task of introducing some much needed reforms in our patent system.

Some time ago, in referring to the hearings of the Oldfield bill for a Revision of the Patent Statutes, I remarked (*Met. and Chem. Eng., Vol. X, 1912, p. 387*):

"Never before was so much direct information collected on the subject of the working of the U. S. patent system. A large number of representative men, including inventors, lawyers, manufacturers and business men, have appeared voluntarily before the House Committee on Patents; they have had ample opportunity to present their views orally and in writing, and the chairman of the committee, Mr. Oldfield, has shown unfailing courtesy and patience to all who appeared before him.

"It is a noteworthy fact that although there clearly exists a great diversity of opinion among the witnesses as to details of proposed reforms, there seems to be a practically unanimous opinion among those who ought to know best, that the defects of the patent system of this country, as it is now, do not reside in the fundamental patent law, but in the way the law is administered before the courts. Lawyers and inventors alike point out that the methods of patent litigation in this country are so absurd, so slow, so complicated and so expensive, that only rich individuals or wealthy corporations can afford to defend a valid patent against infringers, or to contest the validity of a worthless patent.

"From this standpoint, the patent system of the United States is, as has been said, 'a godsend for wealthy corporations, lawyers, and experts.'

"During the hearings it has been pointed out repeatedly how this could be remedied by adopting the methods of England, Germany, and other countries, by eliminating the present absurd system of taking testimony in patent suits and by the creation of a single final court of patent appeals, instead of the nine circuit courts of appeal which may render conflicting decisions, so that a patent is declared valid in one circuit and invalid in another."

Lately, Mr. Oldfield has published his report. (*Report No. 1161, Aug., 1912, from the Committee on Patents, House of Representatives.*) He too lays special stress on the delays and vagaries of court practice in litigation and fully recognizes the evil thereof:

"Two vital changes are essential—the present method of trying patent causes must be abandoned for a new one, and a court of patent appeals must be established.

First. The trial of patent causes.

Nearly all suits involving infringement of patents are tried in the equity courts, where, according to the Federal practice, the testimony is taken and evidence introduced not in the presence of a judge but before an examiner. The duties of the examiner are little more than nominal. He has no power to direct or limit the inquiry, to enforce the attendance of, or answers from, witnesses or the production of other evidence. He can not control the examination or cross-examination of witnesses, or determine the relevancy or value of evidence offered, or the propriety of adding to volume. He does not pass upon the evidence—its character, its weight, or its effect. The court, on the other hand, does not in practice undertake to exercise any supervision over the proceedings conducted before the examiner. The judge who is to hear the case knows little or nothing about it until the printed record embodying the mass of evidence put in before the examiner, and supplemented by printed briefs discussing it, is laid upon the desk when the oral argument begins.

"The examiner, the judicial officer who has seen and heard the witnesses, has no function to perform at the argument or decision of the case; and the judge hears the argument upon evidence which he has not heard, and which he has not read. Often when he hears the argument, he is entirely ignorant too of the art and the trade to which it relates. The issues of fact in the case depend often upon the credibility of witnesses; and everyone recognizes that the credibility of witnesses can not be effectively determined except by those who have seen and heard them. The printed word frequently conveys but an inadequate and incorrect measure of the value of testimony. Decisions rendered under such conditions are apt to be unsatisfactory, but this method of trial results in evils far greater than erroneous decisions.

"The time and money wasted in having testimony given orally before the examiner who does not listen to it, then written out by the reporter, and ultimately printed for submission to the judge, who often does not have time to read all of it, is necessarily great. Days or weeks may be honestly consumed with the introduction of evidence on points which the judge, if present, would declare to be clearly immaterial, or if material, to be adequately established in the absence of evidence to the contrary.

"The fact that no means exist for determining the materiality, propriety or necessity of introducing material evidence in the course of the taking of testimony, results inevitably in great waste of time and money. But the fact that the proceedings before the examiner are practically uncontrolled affords also unequaled opportunity for serious abuse of legal processes—opportunities which are unfortunately availed of all too frequently. Proceedings are often dragged along actively for years, and made to involve expenses so great as to be prohibitive for any but the rich. Powerful trusts, litigating with manufacturers of modest means, have found in those legal proceedings one of the most effective instruments of oppression and of confiscation. Law-

suits conducted under such conditions are apt to result not in determining whether a patent is valid or has been infringed, but whether the limit of endurance has been reached. The immediate result is often a triumph of might over right followed by a rankling sense of injustice and a deep-seated contempt for the law.

"This inefficiency of legal procedure in patent causes tends to accelerate the growth of the trust. Many a small concern has found that it is futile to attempt to seek in the courts redress for infringement of its patents by a powerful trust or that it is disastrous to try to repel a determined attack made under the guise of a patent suit. The small manufacturer yields to the demands of the combination—his poverty and not his will consenting; and relinquishes, often reluctantly, liberty and individuality. On the other hand, when the contest is waged between equal competitors, the long-continued uncertainty due to the necessarily protracted proceedings and the huge expense are apt to suggest combination as a solution of their differences; and in the end they join together in exploiting the public.

"The failure of our law to provide adequate means of determining and enforcing patent rights detracts also greatly from the value of patents to the inventor and other interested persons. It often results also in depriving the public of the benefits which would flow from the development of inventions. This defect in the legal machinery exaggerates the power of the financier. Large capital thus becomes necessary, not for the development of the invention but to protect it. For this reason, the relative value of the required capital as compared with the value of the invention itself is greatly increased, for the most useful invention has been proven to be financially worthless unless buttressed by the large capital necessary to defend the invention legally from attack, either by punishing infringers or by establishing that the invention does not infringe the patents of others. To give due value to an invention in the hands of the inventor or of the small manufacturer, and to insure in the interest of the public the development of all useful inventions, it is essential that an efficient, simple, inexpensive machinery for determining rights under the patent be provided.

"Fortunately, the opportunity for introducing such machinery lies at hand. We have but to follow the methods of trial pursued in patent causes in Germany and in England, which is similar to that prevailing in some of our own States in ordinary equity suits. The evidence should be introduced in open court before the judge who is to hear the argument as soon as the evidence is concluded. The judge is thus in a position to deal promptly and effectively with the whole proceeding. The amount of evidence introduced is greatly lessened because immaterial issues, irrelevant inquiries, impertinent questions may be ruled out. The value of the evidence also may be properly determined because the judge hears and sees the witnesses and may infer from their behavior, intonation, and appearance, as well as from the words spoken, their relative credibility. Litigation which now takes years would, through such a trial, be disposed of in as many months, and where desired could even be disposed of in a few weeks. In the presence of an able judge armed with power to exclude evidence or to enforce its production, and instructed, through his continued presence, in the merits of the controversy, that abuse of the legal process which has become the scandal of the patent practice and one of the most potent instruments of oppression would cease. Justice, swift and more certain, would prevail. Such has been the experience in the disposition of patent cases in England and in Germany, and no less satisfactory results might be expected in America.

"*Second.* Adequate legal machinery demands also the creation of a court of patent appeals.

"The present system under which it is possible that diametrically opposite decisions may be given by the courts of appeal in different circuits, so that the ultimate decision of rights can be determined only after years of litigation, and the allowance of a writ of certiorari to the Supreme Court of the United States, presents further opportunity for oppression by the wealthy and powerful combination.

"In the patent office vital changes also are necessary.

"*Third.* There is great waste of time and expense (which proves a particular hardship to the poor inventor) flowing from interference proceedings designed to determine which of several inventors was the first. The community is really not interested in determining who was the first inventor. The interest of the public is to secure disclosure of the invention. The reward which the public should give in the form of a patent monopoly is to him who makes and first discloses an invention, and every incentive should be given to disclosure at the earliest possible date. The present law gives rather a premium on the withholding of an invention. A man who believes himself to be the original inventor can keep his invention secret, lying by until some other inventor makes application for a patent. A change of the existing rule so as to make the inventor who first discloses, that is, who first files application, the one who is entitled to a patent, would advance the interest of the community and at the same time remove a large part of the evils and oppression incident to the expensive interference proceedings in the Patent Office.

"*Fourth.* Changes should be made in the equipment and organization of the Patent Office to increase its efficiency and to secure for the public and the inventors whom it serves the best possible service. To this end greater opportunities should be afforded the officers and employees of the Patent Office to secure promotion, distinction, and adequate compensation. It should not be necessary for able, faithful, and zealous employees, who are eager to advance the interests of the public, to feel obliged to quit the service in order to secure in private patent practice adequate compensation and recognition of their ability and service.

"If the changes respecting the courts and Patent Office outlined above were made, the public and the inventor would secure further protection from those abuses incident to the great corporations which have been thus described by an eminent inventor, who is the president of the American Institute of Chemical Engineers (Baekeland, THIS JOURNAL, IV, 333):

"'As for wealthy corporations, it has become obvious that the skilful handling of patent cases places them at an untold advantage against their smaller competitors. For them, a well-organized patent department is a reliable machine, where money is the lubricant. This machine, in its slow-but-sure grinding way, can reduce to pulp any of the smaller competitors. For large corporations, the maintenance of such a machine with a staff of lawyers and experts is merely a small side expense. By its aid they can bluff their weaker competitors into quick submission. If this is not successful, they can drag out a patent suit indefinitely, until the weak opponent, unable to bear the ever-increasing expenses, collapses and withdraws.

"'These tactics are well known and have been played successfully, whether it was to uphold a worthless patent or to obtain immunity in case of infringement. In every case, the wealthy corporation is sure of the outcome of the game, and plays, "Heads I win, tails you lose."'

"The Inventors' Guild in its memorial describes the situation as follows:

"'Under existing methods of trying patent causes an inventor-patentee of average means could not, at his own expense, carry to a conclusion an average patent litigation against a wealthy opponent, and, therefore, a few wealthy concerns usually acquire nearly all important patents in their field, to the great damage of the nation, because of the restraint of competition

and because of the resulting tendency of such inventors to seek protection for their inventions by trade secrets or else to cease inventive work'."

Judging from this able and snappy report, there is not the slightest doubt that the public hearings before the Oldfield committee have brought out the most salient vices of our patent system. While presenting this report, Mr. Oldfield has modified considerably his first bill; in fact, he has practically stricken out the original text. Unfortunately, his revised bill does not go at the root of the evil of defective patent litigation, and introduces amendments which, although full of good intentions, carry in themselves dangerous opportunities for clever lawyers to defeat the very purposes for which the bill is intended. Some of the provisions of the bill are so unfortunately worded that they might kill those features of our patent law which aim most at stimulating private research and private enterprise of men of moderate means.

It is an unfortunate fact that most of our legislators, when they speak of patents, have ordinarily in view mechanical patents or secondary inventions: articles like safety razors, alarm-clocks, or other objects of simple description which can readily be identified and understood by an average intelligent man without scientific or technical training. To the public at large, most of these inventions seem merely the result of a lucky inspiration, somewhat in the same way as a lucky prospector finds a gold mine, or a lottery ticket draws the grand prize. Even educated men leave frequently out of sight those far-reaching inventions which involve long years of painstaking and expensive research work, where progress is measured only step by step; where able investigators, sometimes groups of specialists trained in science and technology, devote their lives, their efforts—and often all their cash—to elaborate a difficult industrial problem.

To such a class of inventions belong many of the chemical processes. Yet one of the men of the Congressional Committee on Patents seemed to be under the impression that chemical inventions were mostly intended for the manufacturer of pharmaceutical substances. To the uneducated public, the thought of "patent medicine" enters easily in the mind as soon as reference is made to chemical patents. Few, indeed, realize that some of the chemical processes have brought about far-reaching developments not only in other industries, but in civilization itself; we might mention, for instance, the Goodyear rubber process, which made the automobile possible, the invention of dynamite without which gigantic engineering enterprises like the Panama Canal would be utterly impossible, the cellulose processes, which contributed more to the diffusion of knowledge and culture by the printing press than any other factor, the Bessemer Steel process which furnished us cheaply and abundantly the main raw material for all our engineering, the synthetic processes of the coal tar products which brought forth the most astounding series of applications in therapeutics, surgery, hygiene, art, and general technology, etc., etc. Fewer still are aware that most chemical patents are so-called "process patents," and on this account are least protected against pirating infringers, who always lay in wait for the pioneer, as soon as the latter has, after untiring efforts, succeeded in demonstrating the value of a new process. Only those who have passed through the worry and trying ordeal of pioneership, know what it means to bring to successful issue a new untried chemical process.

Even the theoretical or laboratory chemist, who never was engaged in any industrial pioneer work himself, can hardly conceive that after an invention has been thoroughly studied in the laboratory, nay even after it has been run on a small industrial scale, in most cases, only about ten per cent. of the real work of pioneering has been accomplished. In the majority of cases, lack of funds, lack of manufacturing talent, defective commercial organization, and many other conditions bring forth failure, sorrow and financial loss.

Again, in many instances, it is easier to make the invention and to bring it to technical perfection, than to persuade the public of its advantages. The latter attempt means long tactful and expensive educational work. Unless the pioneer feels that for a short period at least, he may have the absolute monopoly of his inventions, what inducement is there to sacrifice his time and money on a result already too doubtful in itself? Many inventions have gained recognition only *because they were patented* and thus it was worth while to spend money and to show their merits to the public. Other inventions have never received the attention they deserved, because nobody cared to take the risk of educating the public up to them. The metric system was invented by the Arabs many centuries ago, and its benefits are not yet recognized by the business men of this country. If the metric system had been patented, it might, after one generation, have become as popular as "national cash registers."

But just this work of education means, in many cases, an immense amount of money and effort, with all the risks of loss. And then, after you have disclosed accurately your intention in the text of your patent, as the law demands; after you have educated the conservative public to the advantages of your process, then it happens almost regularly that those who at first most strongly denied the advantages of your invention, nay sneered at its claimed possibilities, then simply turn infringers; after every detail of the invention has been carefully explained to them, they calmly declare that there is no invention, and begin to appropriate to themselves all the work of your pioneership. These modern buccaneers have no use for good patent law, or if they tolerate any patent law at all, it must be of such a nature that it can not be enforced. They, too, howl for "patent reform," and unfortunately, howl loudest, but they want patent reform which would kill the best there is in our patent system, and they speak little about reform in court practice. *If our system of court practice had purposely been devised to help the patent pirate, it could not much be improved upon.*

Our laws are painfully strict in protecting so-called "vested property rights," and this protection extends to the most trivial matters. If Tom steals Dick's two-dollar scarf pin, Dick will have no trouble in putting Tom in jail, even if Dick himself has obtained his pin by questionable methods. But when it comes to protecting even for the short period of seventeen years, the most legitimate, the most truly personal property, namely, intellectual property, with all that it involves, with enterprises depending thereon, based often on the work of a lifetime, then our law courts are wofully deficient.

Any system of law which does not adequately protect intellectual property so that rich and poor alike can uphold their rights, is an anachronism in modern civilization.

L. H. BAEKELAND.

ORIGINAL PAPERS

DISTILLATION OF RESINOUS WOOD BY SATURATED STEAM.[1]

By L. F. HAWLEY AND R. C. PALMER.

COMMERCIAL STEAM DISTILLATION PROCESSES.

The steam distillation process for obtaining the volatile oils from the wood of the longleaf pine has been the basis of a small industry since about 1903, being introduced apparently in an attempt to produce wood turpentines at temperatures lower than those used in the destructive distillation processes then in operation, and thus to obtain a product uncontaminated by the decomposition products of wood and rosin. Quite a large number of plants have been built to use either sawmill waste or lightwood, or both, but many have been abandoned, probably only 12 or 15 being in operation in 1911. The quality of the crude turpentine produced has usually been very good, but because this is the only product obtained, or because the yield of this product is often lower than that of "crude turpentines" from other processes, the plants have been successful only under especially favorable conditions.

This process seems to be very promising, however, when combined with other processes for the utilization of the steamed chips, as for instance the extraction of the chips with volatile solvents for the removal of the rosin. Conditions are also favorable for this process in cases where the material would be largely used as fuel or wasted, or is very cheap or so poor in quality that more complicated processes would not be profitable; these conditions are commonly realized in the case of that part of the waste wood of sawmills now used as fuel at the plant or burned on the rubbish pile.

PURPOSE OF INVESTIGATION.

In the fields mentioned above the steam distillation of resinous woods will undoubtedly expand and it was in the hope of promoting this expansion and thus increasing the utilization of a class of material now wasted that this investigation on the fundamentals of the process was undertaken. There has been no uniformity in commercial practice or in the opinions of the various operators and no experimental data have been published on the effects produced by the different readily controlled variables, such as steam pressure, size of chips, or rapidity of distillation. In the methods described in various patent specifications the greatest stress has been laid on the mechanical features of charging and discharging, and of distributing the steam throughout the retort, which, although of great importance in the economy of a commercial method, throw no light on other equally important factors.

There seemed to be, therefore, a profitable field for investigation in determining the relations between the conditions under which the distillation is conducted, on one hand, and on the other hand the amount and kind of products and the readiness with which they are obtained.

THEORETICAL CONSIDERATIONS.

In the description of the experimental work and the discussion of the results it will be necessary to refer constantly to certain theoretical principles which apply to the distillation of volatile oils with steam, and in order to make the future discussions clearer, a brief presentation of these principles is given at this time.

In order to simplify the deductions, the following assumptions are made in regard to the resinous material contained in the "lightwood" from the longleaf pine:[1]

1. It is composed only of turpentine, pine oil,[2] and rosin.

2. The components are all simple substances completely soluble in one another.

3. None of the components are soluble in water.

4. The turpentine and pine oil are both volatile, but the turpentine has the lower boiling point.

5. Rosin is nonvolatile.

While these assumptions are not strictly true in all cases, none of them are sufficiently incorrect to affect seriously the conclusions.

Concerning the distillation with steam of the resinous material defined by the above assumptions, the following deductions can be made:

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

[1] M Vezes (*Bull. Soc. Chim.*, **29**, 470–478 (1903)) has given a very clear and complete discussion of the principles underlying the distillation of the oleoresin from the Maritime pine of France. For the simplification of the discussion the following assumptions were made:

1. That the oleoresin is composed only of essence (turpentine) and colophony (rosin).

2. That these components are both simple substances completely soluble in each other.

3. That neither is soluble in water.

4. That rosin is nonvolatile.

In regard to the oleoresin obtained by chipping the livelong leaf pine tree of the United States, the same assumption can be made, but the oleoresin contained in the pitchy "lightwood" from this species has another component, the heavy, high boiling "pine oil" which must be taken into consideration in the discussion of the steam distillation of such wood.

[2] A discussion of the occurrence of pine oil in the "lightwood" of longleaf pine is given in Forest Service Bulletin **105** ("Wood Turpentines, their Analysis, Refining and Composition," by L. F. Hawley).

1. There will be a separation of the two volatile constituents, the turpentine being in greater proportion in the first part of the distillate and the pine oil in the latter part.

2. The temperature of the distillation under normal pressure will be slightly above 95° C. at the beginning, and will rise throughout the distillation, never quite reaching 100° C., however, as long as any of the turpentine or pine oil remains undistilled.

3. If the pressure at which the distillation is carried on is increased the temperature will be increased, the temperature depending upon the pressure and on the concentrations of the turpentine, pine oil, and rosin; the temperature will, however, never reach the steam temperature corresponding to the pressures used as long as any turpentine or pine oil remains undistilled.

4. The proportion of water to oil in the distillate will increase as the distillation progresses, this proportion being influenced only by the relative amounts of the different constituents present in the oleoresin being distilled.[1]

In these deductions it is considered that the system is in complete equilibrium and under such conditions the behavior of this oleoresin when distilled with steam could be foretold with considerable accuracy, but in the distillation of wood containing the oleoresin, there is a disturbing factor introduced which makes necessary the investigation of the variable mentioned in the introduction. This disturbing factor is the difficulty of keeping a complete equilibrium between the oleoresin and the steam, due to the fact that the wood surrounds the oleoresin and tends to keep the steam from coming in contact with it.

The effects of the size of chips and the rapidity of distillation are not due to a change of the laws governing the distillation of the oleoresin with steam, but to the manner in which they affect the completeness of the equilibrium in the system, or in other words, the completeness of contact between the oleoresin and the steam. In the same way the effects (other than temperature changes) of steam pressure on the results of the distillation are also due to its influence on the completeness of contact between steam and oleoresin rather than to any influence on the behavior of the steam and oleoresin when completely in equilibrium.

EXPERIMENTAL METHODS.

Apparatus and Materials.

The general procedure was to distil charges of the same sized chips under different conditions, and of different sized chips under identical conditions, and to note carefully the variations in the results of the distillations. It was not practicable to make all the runs on exactly comparable material, because a large number of charges of equal resin content could not be secured, and because the material could not be kept without some loss of volatile oil by evaporation. The runs were therefore made in groups with comparable material in each group; the results from each group were made comparable to some extent with those from other groups by a comparison of the resin content of the different groups. This was readily accomplished by distilling the sawdust obtained in the preparation of the material for each group, as this sawdust was a good average sample of the whole group.

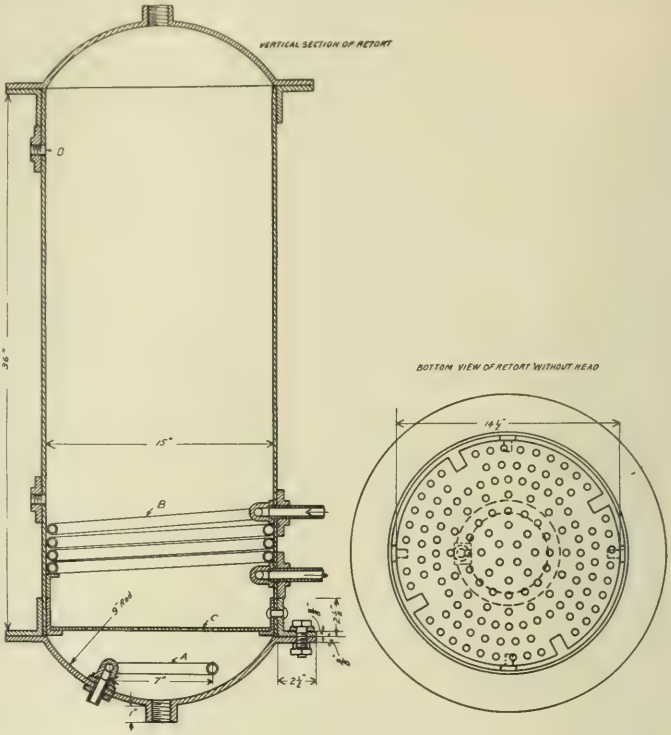

FIG. 1.—Experimental retort.

A sketch of the retort used for the distillations is shown in Fig. 1. This retort was designed for use in extraction of tannin from wood and bark, as well as for distillation experiments; it was therefore made of copper and had the closed steam coils *B*. The perforated plate *C* was designed to hold up the charge while the lower head of the retort was taken off; then by revolving the plate until the slots *E* came opposite the supporting lugs *F*, the plate falls and the charge can be removed. The pressure gage was attached at *D*. The other parts of the retort require no special description. An ordinary copper worm condenser was used and the distillate was caught in 1-liter graduated cylinders.

The J. G. Newman Lumber Co., of Hattiesburg, Miss., furnished for the experiments a large log of pitchy light-

[1] A change in the pressure at which the distillation is carried on might change the proportion of water to oil in the distillate but this change would be only slight and there is not sufficient data available to decide even the direction of this change.

wood in which the pitch was distributed with unusual evenness. From this log it was possible to prepare a number of charges of chips, of which all from one portion of the log were similar in resin content.

Preparation of Material.

The method of selecting material so that each charge should be comparable with the other charges in the same group is shown in Table I and Fig. 2. The

Table I.—Experimental Runs Made and Material Used in Each.

Group No.	Run No.	Block.	Material used. Sticks.	Sections.	Size of chips.	Remarks.
					Inches.	
I	1	A	.....	.....	Sawdust	Obtained in cutting sections.
	2	A	.....	.....	"	"
	3	A	.....	.....	"	"
	4	A	I to VII...	10, 22, 28.....	1 x 1	
	5	A	I to VII...	6, 18, 29.....	1/4 x 1/8	
	6	A	I to VII...	4, 17, 30.....	1/2 x 1/4	
	7	A	I to VII...	2, 14, 25.....	1/4 x 1/8	
	8	A	I to VII	3, 5, 9, 11...	1/4x1/8	Chips from each section divided among the three runs.
	9	A		13, 15, 19 21		
	10	A		23, 26, 27, 31		
II	11	A	.....	.....	Sawdust	Obtained in sawing slabs.
	12	A	.....	.....	1 x variable	Sections of slabs.
	13	..	.....	.....	6 x same	
					Inches.	
III	14	A	I to VII...	1, 7, 8, 12, 16 1/32 of section		One-half of each section used in each run.
	15	A	I to VII	20, 24, 32, 33 1/2 of section		
IV	16	B	.....	.....	Sawdust	Obtained in cutting sections.
	17	B	I to VII...	All odd numbers	1/4 x 1/8	Chips from each section divided between each run.
	18	B	I to VII...			
	19	B	I to VII...	All even numbers	1/2 x 1/2	"
	20	B	I to VII...			
V	21	C	.....	.....	Sawdust	Obtained in cutting sections.
	22	C	I, IV, VII.	1, 4, 7, 10.....	2 x 2	
			III, VI....	2, 5, 8, 11.....		
			II, V.....	3, 6, 9, 12.....		
	23	C	III, VI....	1, 4, 7, 10.....	2 x 2	
			II, V.....	2, 5, 8, 11.....		
			I, IV, VII.	3, 6, 9, 12.....		
	24	..	II, V.....	1, 4, 7, 10.....	4 x 4	
			I, IV, VII.	2, 5, 8, 11.....		
			III, VI....	3, 6, 9, 12.....		
VI	25	D	.....	.....	Sawdust	Obtained in cutting sections and in slabbing blocks
	26	D	I to VIII..	1, 4, 6, 9.....	1 x 1	Obtained in cutting sections.
	27	D	I to VIII..	2, 5, 8.....	1 x 1	
	28	D	I to VIII..	3, 7.....	1 x 1	
VII	29	E	.....	.....	Sawdust	
	30	E	I, V.....	1, 5, 9, 13.....		Shavings
			II, VI....	4, 8, 12, 16....		
			III, VII...	3, 7, 11, 15....		
			IV.....	2, 6, 10, 14....		
	31	E	I, V.....	3, 7, 11, 15....		"
			II, VI....	2, 6, 10, 14....		
			III, VII...	1, 5, 9, 13.....		
			IV.....	4, 8, 12, 16....		
	32	E	II, V.....	2, 6, 10, 14....	1/2 x 1/2	
			II, VI....	1, 5, 9, 13.....		
			III, VII...	4, 8, 12, 16....		
			IV.....	3, 7, 11, 15....		
	33	E	I, V.....	4, 8, 12, 16....	1/2 x 1/2	
			II, VI....	3, 7, 11, 15....		
			II, VII....	2, 6, 10, 14....		
			IV.....	1, 5, 9, 13.....		

sticks were sawed into sections at one time, but usually the sections were chipped only as required; that is, just before each distillation. Thus the sections for the last runs of a group had been longer cut than those of the first runs, and although they were kept in covered cans, or if without cover were piled close together, there was still some chance of loss by volatilization, especially when some time intervened, as in the large number of runs in Group I. To lessen the loss by volatilization during the chipping process, the chips were covered with water as fast as they were made. The sawdust charges were put into the retort without any delay after collection, except in runs 2 and 3, which were prepared and collected but not distilled at the same time with run 1.

Distillation.

Only a general description of the procedure will be given here; the same general methods were used in all cases and the details are given later in the tabulated record of the runs.

Regulation.

The speed and pressure of the distillations were regulated simply by the inlet valve at the bottom and by the outlet valve at the top of the retort. During distillation at atmospheric pressure the outlet valve was left open and the speed regulated by the inlet valve alone; but during distillation at higher pressure it was, of course, necessary to use both valves in order to keep both speed and pressure at the required values. The variation in speed was never more than one-half minute per liter of distillate, and in pressure never more than 2 pounds per square inch from the required values.

Data Obtained.—A typical data sheet giving an example of the records obtained in each distillation is shown in Table II. The distillate was caught in one-liter fractions and the time and pressure were recorded with every fraction. The amount of oil in each liter of distillate was determined as accurately as possible while in the original receiver (one-liter cylinders graduated to 10 cc.); the oil was then separated from the water in a separatory funnel and its specific gravity determined. When the amount of oil in the fractions was so small that a specific gravity determination could not readily be made on a single fraction, the oil from a sufficient number of fractions was combined to make the determination possible. As a check on the total amount of oil computed from the rough measurements on the separate fractions, the combined oil from all the fractions or from the fractions of different portions of the distillation was accurately measured.

The detailed records for each distillation will not be given in this report, but instead the essential part of this data will be tabulated together with other factors computed from the data. The discussion of the data from all groups will be taken up together after the experimental work has been described.

End Point.—It will be noticed in Table II that the amount of oil in one liter of distillate gradually decreased and decreased very slowly toward the end of a distillation. On this account it became necessary to arbitrarily choose a ratio of oil to water which might be considered as the end of a distillation under one set of conditions in order to make the results of differ-

ent distillations comparable and at the same time to keep the time required within practicable limits. In the first five runs the end point was too high and too variable, since it was not recognized that the end point must be very carefully regulated in order to obtain comparable results. These first five runs are, therefore, not comparable with those which follow, in which the end point was carefully regulated at somewhat lower values. It was also found that after distilling a charge under one set of conditions until a certain end point was reached, if the distillation was as important until after Run 5 was finished, so that for another reason Runs 1 to 5 are not comparable with those which follow.

The proper end point for any distillation after Run 5 was considered to be reached only when the required ratio of oil to water in the distillate had been attained both before and after interruption of the distillation.

DISCUSSION OF RESULTS.

The data obtained by the distillation of the various runs are given in Table III, together with the condi-

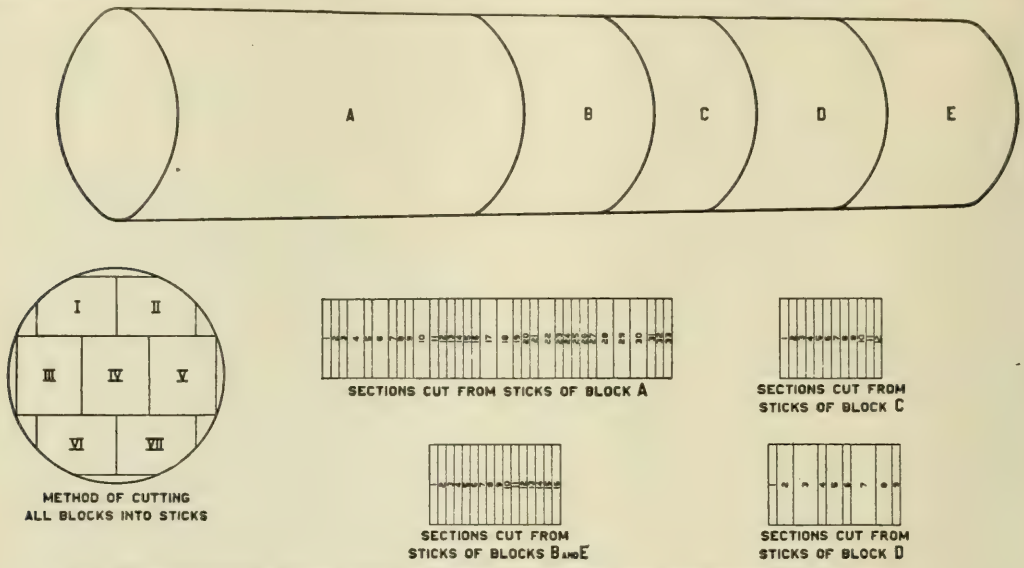

FIG. 2.—Diagram showing method of cutting up material. (In thickness the sections are drawn to scale, the smallest being 1 inch thick.)

interrupted for an hour or more and then continued under the same conditions as before, a further supply of oil could be obtained before the same end point was reached again. This additional amount of oil obtained as a result of interrupting the distillation amounted to from 2 per cent. to 18.8 per cent. of the oil already obtained before the distillation was interrupted. The highest increases in yields due to this manipulation were those runs where there was still considerable oil present in the wood when the distillation was interrupted (although, of course, all the oil possible had been removed under the prevailing conditions). For instance, in Runs 14 and 15, after all the oil possible had been distilled at 50 pounds pressure, interruption of the distillations over night made it possible to distil respectively 18.8 per cent. and 15.1 per cent. more oil under the same conditions; in both these cases there was still considerable oil present in the wood as shown by further distillation at increased pressures. In Runs 11 and 21, however, after all the oil possible had been distilled at atmospheric pressure, interruption of the distillations made it possible to obtain only 2.9 per cent. and 4.0 per cent. more oil under the same conditions; in these cases there were much smaller quantities of oil left in the wood than in Runs 14 and 15. This effect also was not recognized tions under which the distillations were made. In the table the size of the chip as given in column two is expressed in inches with the length parallel to the grain given first. The values given in the columns headed "yield" are expressed in cc. of oil per pound of wood. The possible error in these determinations of yields is apparently about 6 to 7 per cent. and is due to difficulties in sampling, in regulating evaporation during the preparation of material, and in obtaining comparable end points in different distillations.

An example of results which must be due to such errors is seen in Runs 23 and 24. The chips in Run 24 are larger than those in Run 23 and the yield should be perhaps less and certainly not greater from the larger chips, and yet the yields obtained from Run 23 are 5.0 per cent. less than those from Run 24. Another similar example is shown in Runs 30 and 31. It might be thought that some of these variations in yields were due to incomplete distillation caused by the "channeling" of the steam through the charge in such a way that part of the wood was never touched by the steam, but in several runs after all the oil possible had been distilled under some one set of conditions the top of the retort was removed, the charge well stirred, and the distillation continued under the

same conditions as before without any indications that the stirring had discovered undistilled material in the charge. It seems probable, therefore, that with a retort of the shape and size used in these distillations, the effect of incomplete distillation due to in-

TABLE II.—TYPICAL DATA SHEET, ILLUSTRATING THE RECORDS TAKEN OF THE DISTILLATIONS.

Project 123—Run No. 23. Chips 1″ × 2″ × 2″.

Weight of can + water—	160 lbs.
Weight of can + water + chips—	215 lbs.
Weight of chips—	55 lbs.
Steam turned on	9.23
Distillate began to flow—	9.28.30

Time. Hrs.	Time. Min.	Liters of distillate.	Cc. of oil in distillate.	Cc. of oil total computed.	Cc. of oil total determined.	Specific gravity of oil.	Pressure.
9	36	1	88	88		0.8810	70
9	48	2	154	242		0.8794	72
9	59½	3	110	352	362	0.8851	71
10	8	4	73	425		0.8944	71
10	17	5	60	485			68
10	29½	6	55	540		0.8980	71
10	40½	7	50	590			70
10	51½	8	44	634		0.8981	72
11	½	9	39	673			70
11	8½	10	24	697		0.9010	69
11	18½	11	27	724			72
11	28	12	26	750			69
11	38	13	19	769			72
11	47½	14	22	791		0.9016	68
11	57½	15	17	808	....		69
12	7	16	17	825	839		69
12	17	17	16	841			69
12	27½	18	16	857		0.8987	72
12	38½	19	18	875			72
12	50	20	19	894			64
1	0	21	15	909			71
1	9	22	13	922		0.8965	72
1	18½	23	11	933	——		71
1	27½	24	10	943			69
1	39	25	12	955	979		68
1	48	26	10	965			70
2	0	27	11	976			70
2	11½	28	10	986			68
2	23½	29	12	998		0.9858	72
2	34½	30	8	1006			73
2	45½	31	8	1016			72
2	56½	32	10	1026	1047		63
3	7½	33	13	1039			45
3	17	34	6	1045			32
3	26½	35	5	1050			20
3	37	36	4	1054		0.8936	12
3	43	37	1	1055			4
3	45	38	1	1056	1095		0
Distillation interrupted over night.							
9	23½	39	22	1078		0.8934	72
9	35	40	17	1095			73
9	46	41	15	1110			71
9	46	41	15	1110			71
9	57	42	10	1120		0.9003	72
10	8	43	9	1129			70
10	19	44	8	1137			72
10	30	45	7	1143			58
10	43	46	15	1158			34
10	53	47	8	1166		0.8935	19
11	4	48	6	1172			6
11	6	49	2	1174	1235		0

No. of liters.	Yield cc. lb.	Efficiency.
16	15.3	0.95
25	17.8	0.71
38	19.9	0.51
49	22.4	0.46

complete contact between the steam and the surface of the chips is negligible.

The values given under "efficiency" are obtained by dividing the yields per pound of wood by the number of liters of total distillate, the efficiency factor being cubic centimeters of oil per pound of wood per liter of distillate or $\frac{\text{cubic centimeters oil}}{\text{pounds wood} \times \text{liters distillate}}$. It might be thought that this "efficiency factor" would have more significance if it represented only the relation between oil and total distillate, but, as will be seen later,[1] this relation would be affected by the amount of wood distilled. Of course, the effect may not be in exact proportion to the amount of wood distilled as represented in the factor used, but it is thought that more nearly comparable efficiency factors are obtained by including the amount of wood as above. These factors represent approximately the relative amounts of oil obtained in the different runs per unit of steam consumed, exclusive of the steam which supplies the heat lost by radiation.

EFFECT OF SIZE OF CHIP ON YIELD AND EFFICIENCY.

In general, other conditions being the same, the smaller the chip, the larger the yields and the higher the efficiency. This is shown in Table IV, which contains selected data from Table III. Four groups of distillations are given, in each of which all the other conditions except size of chip are as nearly as possible the same, and in every case the smaller-sized chips show the larger yield and higher efficiency. The effect on yield is not so marked in the case of Runs 26 and 27 (and some of the other runs given in Table III), but this is accounted for by the fact that the pressure was high enough so that nearly all the oil was removed even from the larger-sized chips. In the case of two runs in which all the oil was removed even from the larger chips, the yields would of course be the same, but the efficiency would probably be higher with the smaller-sized chips.

EFFECT OF PRESSURE ON YIELD AND EFFICIENCY.

In general, other conditions being the same, higher pressures give larger yields without lowering the efficiency. This is shown in Table V, which gives three groups of runs, in each of which all conditions except steam pressure are as nearly as possible the same. In all cases the higher steam pressure produced the larger yield and with the same or higher efficiency. The effect of pressure on yields is also shown in another way in many of the runs in Table III, in which, after obtaining all the oil possible by distilling under one pressure, a further yield of oil was obtained by continuing the distillation under a higher pressure.

EFFECT OF SPEED OF DISTILLATION ON YIELD AND EFFICIENCY.

Other conditions being the same, increased speed of distillation decreases both the yield and the efficiency. This is shown clearly in Table VI, which gives the results of two sets of two runs each, all the conditions except the speed being the same in each set. The more rapid passage of the steam through the charge probably causes it to be less saturated with the oil vapors, thus directly decreasing the efficiency. The yield is decreased probably because the same end point is reached sooner when the steam is less completely saturated. This is indicated by the more nearly equal total yields obtained in each set of runs by finishing up the distillations at the same pressure

[1] The same reasoning as is given on page 794 regarding the effect of the size of retort on the efficiency applies also to the effect of the amount of wood distilled on the efficiency.

TABLE III.—SUMMARY RECORD OF EXPERIMENTAL RUNS.

Group No.	Run No.	Size of chips	0 lbs. pressure: Yield cc. per lb.	0 lbs. pressure: Efficiency.	20 and 30 lbs. pressure: Yield cc. per lb.	20 and 30 lbs. pressure: Efficiency.	40 and 50 lbs. pressure: Yield, cc. per lb.	40 and 50 lbs. pressure: Efficiency.	70 lbs. pressure: Yield cc. per lb.	70 lbs. pressure: Efficiency.	Total: Yield, cc. per lb.	Total: Efficiency.	Speed, min. per liter.	End point, cc. per liter.
	1	Sawdust	20.6	1.71	....		9.92	0.45			30.8	0.90	4	25 and 12
	2	Sawdust	.	.	.		32.7[3]	1.26			32.7	1.26	4	18
	3	Sawdust	12.5	1.56	....		8.24	0.41			20.7	0.74	4	17 and 12
	4	2" × 1" × 1"	.	.	.	.			20.3	0.33	20.3	0.33	5	12
I.	5	2" × [illegible] × 1/8"	6.4	0.61	5.8	0.45	3.93	0.33	9.1	0.33	25.2	0.38	4	12
	6	2" × [illegible] × 1/4"	8.0	0.55	5.1[1]	0.28	6.1[3]	0.24			19.2	0.34	10	10
	7	1" × [illegible] × 1/8"	15.7	0.63	4.6[1]	0.29	5.33	0.14			25.6	0.40	10	10
	8	1" × 1/2" × 1/4"	10.2	0.46	6.5[1]	0.25	6.2[3]	0.19	.	.	23.0	0.29	10	10
	9	1" × [illegible] × 1/4"	.	.	22.4[2]	0.46	3.0[4]	0.19	4.5	0.21	29.9	0.34	10	10
	10	1" × [illegible] × 1/4"	.	.	....		27.2[4]	0.46	1.5	0.12	28.7	0.40	10	10
	11	Sawdust	27.7	1.46	.	.	2.0[3]	0.25	.	.	29.7	1.1	10	10
II.	12	1" × Variable	.	.	....	.	.	.	25.7	0.49	25.7	0.49	10	10
	13	6" × Variable	.	.	....	.	.	....	12.3	0.29	12.3	0.29	10	10
III.	14	1" × 5" × 8"	....	....	....	.	19.7[4]	0.35	5.9	0.17	25.6	0.28	10	10
	15	1" × [illegible] × 1 1/2"	....	....	.	.	24.5[4]	0.41	4.7	0.15	29.2	0.32	10	10
	16	Sawdust	25.2	0.97	....	.	4.0[3]	0.31	....	....	29.1	0.75	10	10
	17	1" × 1/4" × 1/8"	....	....	24.5[2]	0.50	.	.	....	....	....	....	10	10
IV.	18	1" × [illegible] × 1/8"	.	.	....	....	26.8[4]	0.50	....	....	....	....	10	10
	19	1" × 1/2" × 1/8"	....	....	....	.	25.3[4]	0.55	....	....	....	....	10	10
	20	1" × 1/2" × 1/2"	....	....	....	.	....	.	29.8	0.63	29.8	0.63	10	10
	21	Sawdust	24.6	1.05	....	.	1.7[3]	0.23	....	....	26.3	0.82	10	10
V.	22	1" × 2" × 2"	....	....	....	.	....	....	23.1	0.39	23.1	0.39	10	10
	23	1" × 2" × 2"	....	....	....	.	....	.	22.4	0.46	22.4	0.46	10	10
	24	1" × 4" × 4"	.	....	....	.	....	....	23.6	0.44	23.8	0.44	10	10
	25	Sawdust	24.0	0.89	....	....	2.6[3]	0.26	....	....	26.6	0.70	10	10
VI.	26	1" × 1" × 1"	....	....	....	....	....	....	22.8	0.45	22.8	0.45	10	10
	27	2" × 1" × 1"	....	....	....	....	.	....	21.4	0.31	21.4	0.31	10	10
	28	3" × 1" × 1"	....	....	....	....	....	.	12.9	0.29	12.9	0.29	10	10
	29	Sawdust	19.3	0.84	....	....	1.7[3]	0.17	....	....	21.0	0.64	10	10
	30	Shavings	18.8	0.94	....	....	....	....	....	....	....	....	6	5
			0.6	....	....	....	.	....	....	....	....	....	10	7
			19.4	0.85	....	....	....	....	....	....	....	....	6 and 10	5 and 7
			....	....	....	....	3.1[3]	0.39	....	....	....	....	10	10
			....	....	....	....	....	....	....	....	22.5	0.73	6 and 10	5 and 7
VII.	31	Shavings	16.0	0.84	....	....	....	....	....	....	....	....	3	5
			1.4	....	....	....	....	....	....	....	....	....	10	7
			17.4	0.70	....	....	....	....	....	....	....	....	3 and 10	5 and 7
			....	....	....	....	3.8[3]	0.38	....	....	....	....	10	10
			....	....	....	....	....	....	....	....	21.2	0.60	3 and 10	5 and 7
	32	1" × 1/2" × 1/2"	....	....	....	.	....	....	20.1	0.43	....	....	6	5
			....	....	....	....	....	....	0.7	....	....	....	10	7
			....	....	....	....	....	....	20.8	0.39	20.8	0.39	6 and 10	5 and 7
	33	1" × 1/2" × 1/2"	....	....	....	....	....	....	18.1	0.39	....	....	3	5
			....	....	....	....	....	....	2.2	....	....	....	10	7
			....	....	....	....	....	....	20.3	0.33	20.3	0.33	3 and 10	5 and 7

[1] = 20 lbs. [2] = 30 lbs. [3] = 40 lbs. [4] = 50 lbs.

but at lower speeds. The variation in efficiency is not, however, as might be expected, exactly proportional to the speed, since doubling the speed decreases the efficiency by only about 10 per cent. from 0.94 to 0.84 in Runs 30 and 31, and from 0.43 to 0.39 in Runs 32 and 33.

TABLE IV.—EFFECT OF SIZE OF CHIP ON YIELD AND EFFICIENCY.

Run No.	Size of chip.	Pressures.	Yields.	Efficiency.	End point, Speed, min. per liter.	End point, cc. oil per liter distillate.
7	1" × [illegible] × 1/8"	Atmospheric	15.7	0.63	10	10
8	1" × 1/2" × 1/4"	Atmospheric	10.2	0.46	10	10
12	1" sections from slabs	70 pounds	25.7	0.49	10	10
13	6" sections from same	70 pounds	12.3	0.29	10	10
14	1" × 5" × 8"	50 pounds	19.7	0.35	10	10
15	1" × 1 1/2" × 1 1/2"	50 pounds	24.5	0.41	10	10
26	1" × 1" × 1"	70 pounds	22.8	0.45	10	10
27	2" × 1" × 1"	70 pounds	21.4	0.31	10	10
28	" × 1" × 1"	70 pounds	12.9	0.29	10	10

If, as seems probable, the effects of speed are due to the variations in the time during which the steam is in contact with the wood, then the size of the retort would have a similar effect, that is, a speed of 10 minutes per liter in a certain sized retort would be equivalent to 5 minutes per liter in a retort twice as large, since a unit of steam would be in contact with a unit of wood for the same length of time in either case.

RELATIONS BETWEEN END POINT, YIELD AND EFFICIENCY.

As shown in Table II, the amount of oil in a liter of total distillate is greatest at the beginning of the distillation and decreases steadily as the distillation

TABLE V.—EFFECT OF PRESSURE ON YIELD AND EFFICIENCY.

Run No.	Size of chip.	Pressures.	Yields.	Efficiency.	End point, Speed, min. per liter.	End point, cc. oil per liter distillate.
8	1" × 1/2" × 1/4"....	Atmospheric	10.2	0.46	10	10
9	1" × 1/2" × 1/4"....	30 pounds	22.4	0.46	10	10
10	1" × 1/2" × 1/4"....	50 pounds	27.2	0.46	10	10
17	1" × 1/4" × 1/8"...	30 pounds	24.5	0.50	10	10
18	1" × 1/4" × 1/8"...	50 pounds	26.8	0.50	10	10
19	1" × 1/2" × 1/8"....	50 pounds	25.3	0.55	10	10
20	1" × 1/2" × 1/2"....	70 pounds	29.8	0.63	10	10

progresses, except when the conditions of distillation are changed, and then the increase in the amount of oil per liter is usually only slight and temporary. This was true in all the distillations and it is evident, therefore, that the efficiency factor will decrease steadily throughout the distillation and its final value will

depend on the end point used. Therefore, the efficiency can be increased by stopping the distillation before all the oil possible has been obtained and thus decreasing the total yield of oil. For the same reason the efficiency will be decreased by continuing the distillation until all the oil possible has been obtained and thus increasing the total yield of oil. For instance, in Run No. 23 (Table III) if the distillation had been stopped with an end point of 12 cc. per liter, at the 25th liter the yield would have been only 15.3 cc. per pound while the efficiency would have been 0.95. By continuing the distillation until the end point (after an interruption of the distillation) was 10 cc. per liter, a much larger yield, 22.4 cc. per pound, was obtained, but only at the expense of a much decreased efficiency (0.46).

TABLE VI.—EFFECT OF SPEED ON YIELD AND EFFICIENCY.

Run no.	Size of material	Pressure,	Speed, min. per liter.	End point, cc. oil per liter.	Yield.	Total yield.	Efficiency.	Total efficiency.
30	Shavings	Atmospheric	6	5	18.8	18.8	0.94	0.94
		Atmospheric	10	7	0.6	19.4	....	0.85
		40 pounds	10	10	3.1	22.5	0.39	0.73
31	Shavings	Atmospheric	3	5	16.0	16.0	0.84	0.84
		Atmospheric	10	7	1.4	17.4	....	0.70
		40 pounds	10	10	3.8	21.2	0.38	0.60
32	1″ × ½″ × ½″ ..	70 pounds	6	5	20.1	20.1	0.43	0.43
			10	7	0.7	20.8	....	0.39
33	1″ × ½″ × ½″...	70 pounds	3	5	18.1	18.1	0.39	0.39
			10	7	2.2	20.3	....	0.33

THE PRESSURES REQUIRED TO DISTIL COMPLETELY DIFFERENT SIZES OF MATERIAL.

Sawdust.—The volatile oil cannot be completely distilled at atmospheric pressure even from a material as finely divided as sawdust. This can be seen from Runs 11, 16, 21, 25 and 29 (Table III) in which, after removing all the oil possible at atmospheric pressure, a further distillation at 40 pounds pressure removed from 6.6 to 15.8 per cent. more oil. It was found that after distilling at 40 pounds pressure a further distillation at 70 pounds was without appreciable effect. It can be safely stated that 40 pounds pressure is sufficient for the removal of all the volatile oil from material as small as sawdust. It is possible that lower pressures might give almost as good results, but this point cannot be determined from the data on hand.

Chips 1″ × 1/4″ × 1/8″.—This size material cannot be completely distilled at 30 pounds pressure (Run 17) and probably not at 50 pounds pressure (Run 18). In Run 18 the yield obtained from chips 1″ × 1/4″ × 1/8″ is almost the same, within the limit of possible variation, as from the sawdust of Run 16, but apparently not quite all the oil has been removed.

Chips 1″ × 1/2″ × 1/2″.—Chips of this size cannot be completely distilled at 50 pounds pressure (Run 19), but can at 70 pounds (Runs 20, 32, and 33).

Chips larger than 1″ × 1/2″ × 1/2″.—At the maximum pressure used, 70 pounds, chips larger than 1″ × 1/2″ × 1/2″ cannot be completely distilled, but as the size of chips is increased there is no sudden drop in the yields obtainable at this pressure until sizes larger than 2 inches with the grain (Runs 27 and 28)[1] and 4 by 4 inches across the grain are used (Runs 14 and 24). It is probable that 80 to 85 per cent. of the oil could be removed from chips 2″ × 4″ × 4″ by distillation at 70 pounds pressure.

EFFECT OF PRESSURE ON COMPOSITION OF OIL.

Analyses were made by the method described in Forest Service Bulletin **105** of part or all of the oil from each of the runs, but there was not enough difference between the various samples so that all of the analyses will need to be given. A few distillation curves showing the main points of interest will be given.

Pine Oil.—The proportion of pine oil in the crude turpentine did not vary except in cases which could be explained by variation in other factors besides pressure and, therefore, so far as the results show, the pressure has no influence on the proportion of pine oil except the influence due to increasing the total yields. In all cases where the total oil obtained was analyzed, and where the oil was nearly completely removed from the wood, the percentage of pine oil by weight varied only between 48 per cent. and 52 per cent.[2] In cases where only part of the oil was removed by the distillation, as in Run 4, the proportion of pine oil was less.

Dipentene.—The detection of small differences in the proportion of dipentene present cannot be made by the method of examination used, especially when such large proportions of pine oil are present. There seemed to be, however, more dipentene in the crude turpentines produced at higher pressures. Figs. 3 and 4, representing the distillation curves obtained in the analyses of the oils from Runs 21 and 23, respectively, illustrate this point. The oil obtained from sawdust mostly at atmospheric pressure (Fig. 3) apparently contains less dipentene than the oil distilled entirely at 60 pounds pressure (Fig. 4), the specific gravity values being lower and the proportion of the oil boiling between 165° and 180° larger in the latter case. It had formerly been thought that the dipentene which had been found in wood turpentines was caused by the temperature used in distilling the oil from the wood, but indications of dipentene were found in all the samples of oil obtained in this investigation, even in those produced at atmos-

[1] In determining the percentage of total oil obtained in the runs of Group VI it must be remembered that the sawdust of Run 25 was not exactly a representative sample of the material of that group but that it was mixed with the sawdust obtained in cutting the slabs from the blocks. In several cases similar samples of sawdust obtained in cutting the slabs had been distilled and found to contain more volatile oil than the sawdust obtained in cutting the blocks. It is probable, therefore, that the proportion of volatile oil in the mixed sample of sawdust was somewhat greater than in the rest of the material in this group. This point is further indicated by a comparison of the yields obtained from the sawdust runs in the different groups. With the exception of Group VI (Run 25) the yields from the sawdust decrease, as might be expected, for the reason that the material for the groups was cut from the same log in order of the group number, beginning at the butt end and the content of volatile oil in the butt end was higher than in the upper portions of the log. It is probable, therefore, that a value of 24 to 25 cc. oil per pound of wood would more nearly represent the volatile oil content of the group.

[2] Exceptions were found to this in the oils from Group II which contained about 28 per cent. pine oil. But the material for this group did not represent a complete cross section of the log, being composed instead only of the outside pieces, the slabs. The outer layers of this log evidently contained a smaller proportion of pine oil than the rest of the wood.

pheric pressure, and it is very probable that dipentene was present as such in the wood distilled. In order to make sure that this material with low specific gravity and high boiling point was dipentene and not some other terpene with similar physical properties, a chemical examination was made of the fractions 165° to 185° from some of the turpentines produced at atmospheric pressure and dipentene was identified by means of the tetrabromide, m. p. 125°–126°.

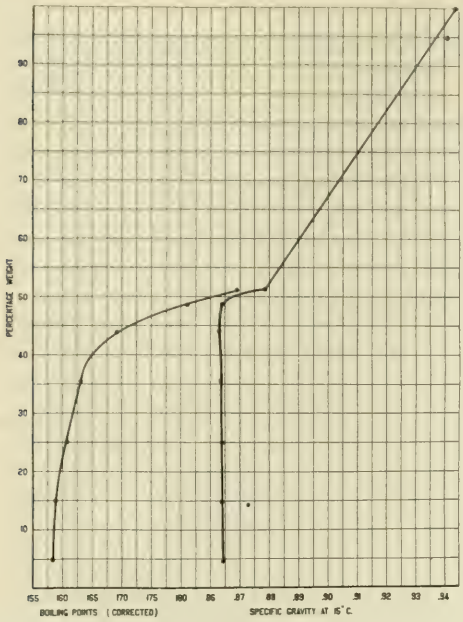

FIG. 3.—Boiling point and specific gravity curves for oil from Run 21.

In order to determine the possibility of the transformation of pinene into dipentene under the condition of steam distillation the sawdust from Run 29 was air-dried and moistened with 1175 cc. of gum turpentine (an amount equal to the total volatile oil originally present) and distilled at atmospheric pressure. The oil, on analysis, showed no indications of dipentene. The experiment was repeated, making the distillation at 50 pounds pressure, but with the same result. These results preclude the possibility of formation of dipentene from pinene under the conditions of steam distillation pressures below 50 pounds and indicate very strongly that dipentene occurs as such in lightwood.

Light Oils.—Figs. 3 and 4 also illustrate another effect of pressure on the composition of the crude turpentines. In these analyses, as in many others, the crude turpentines produced at pressures as high as 70 pounds show a considerably higher value for the specific gravity of the first fraction than do the turpentines produced at lower pressures. This indicates that some substance with low boiling point and high gravity (above 0.870 at 15° C.) is produced at the higher pressures; this substance might come from the incipient decomposition of some portion of the resin at the temperature to which it is subjected. The first fractions from the analyses which contained this substance were slightly yellow and had a peculiar odor, different from the rest of the fractions. A treatment with caustic soda reduced the gravity of these fractions but increased the yellow color. It was found, however, that by the treatment of a turpentine like that shown in Fig. 4 with caustic soda followed by a distillation it was possible to prepare a refined turpentine which showed no abnormality of the first fraction in color, odor, or gravity. The presence of this substance should not, therefore, introduce any difficulty in the refining process.

Another test for the presence of decomposition products was made on several of the samples produced at different pressures by treating the oil with concentrated hydrochloric acid; a red color produced in this

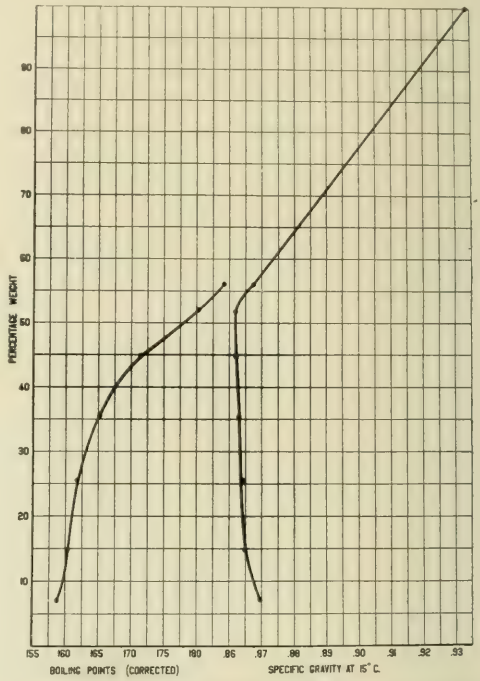

FIG. 4.—Boiling point and specific gravity curves for oil from Run 23.

way is supposed to indicate the presence of rosin oil. There was only a very slight coloration of the oils produced at atmospheric pressure, but this coloration increased with the pressure, becoming very marked in the oils produced at 50 pounds and 70 pounds pressure.

FRACTIONATION OF THE OIL DURING DISTILLATION.

Some very interesting conclusions regarding the details of the manner in which the volatile oil leaves the wood can be obtained by comparing the values of the specific gravity of various portions of the distillate. As was previously stated, the specific gravity of the oil was determined from each liter of distillate, or from as many liters as were necessary to furnish the

amount of oil required for a determination. Figs. 5, 6 and 7 show these values of the specific gravity obtained in Runs 16, 20 and 7, respectively, plotted against the percentages of the total oil obtained.

Fig. 5 shows the changes in the specific gravity of

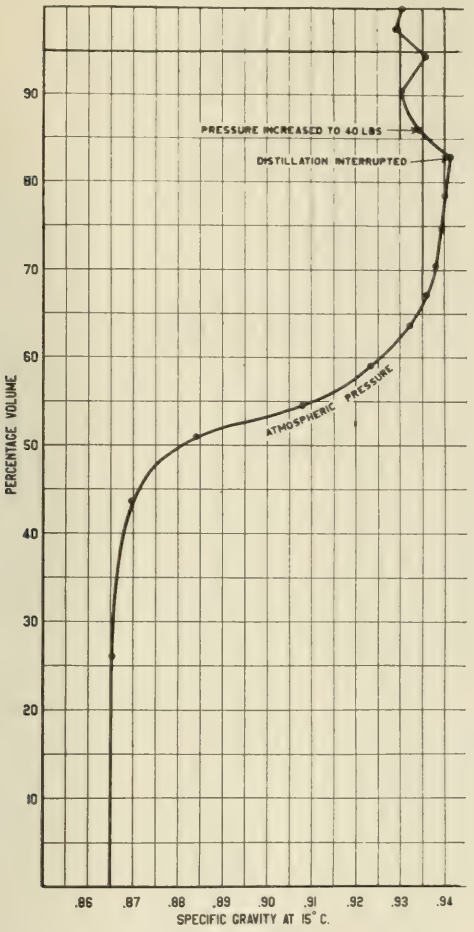

FIG. 5.—Curve showing fractionation of oil during Run 16.

the oil obtained during the distillation of a charge of sawdust, first at atmospheric pressure and then at 40 pounds pressure. The first portions of the oil were nearly pure turpentine, but after about 44 per cent. had been distilled the gravity increased rapidly, indicating the presence of pine oil in increasing quantities; when the distillation was from about 67 per cent. to 83 per cent. completed the oil was nearly pure pine oil. The part of the curve up to 83 per cent. resembles very closely the distillation curve which could be obtained from the distillation with steam of a crude turpentine; that is, the presence of the wood seems to have no effect on the manner in which the volatile oils are distilled. A difference is seen, however, in that portion of the curve beyond 83 per cent.; after practically all the oil possible had been removed by a continuous distillation at atmospheric pressure, the interruption of the distillation followed by a further distillation under the same pressure produced a small further yield of oil with a lower gravity, and on increasing the steam pressure, still more oil was obtained with a still lower gravity. This indicates that both the interruption of the distillation and the increase in steam pressure brought more oil into contact with the steam and that this oil contained some of the low-gravity turpentine material.

A very different behavior is shown in Fig. 6, which represents the distillation of chips $1'' \times 1/2'' \times 1/2''$ at a pressure of 70 pounds. In distillation under these conditions there was much less tendency for the oil to be separated as it is distilled, the gravity of the very first fraction being higher than that of pure tur-

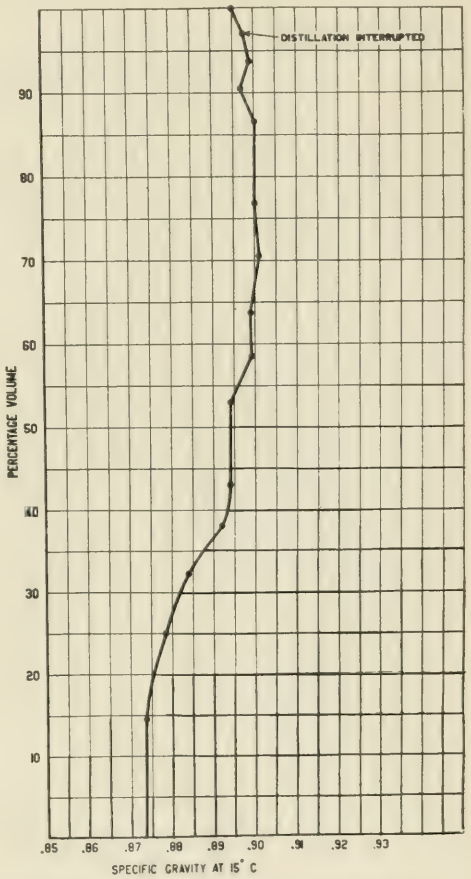

FIG. 6.—Curve showing fractionation of oil during Run 20.

pentine and the gravity of the later fractions never reaching that of pure oil; that is, the turpentine and pine oil distilled together throughout the run. This indicates that new supplies of volatile oils were brought into contact with the steam more or less continuously throughout the distillation, since otherwise the turpentine would have distilled first and the last fractions would have been nearly pure pine oil.

A still more striking picture of the variation in the

gravity of the distillate due to changes in the conditions of distillation is shown in Fig. 7; this represents the gravities of different parts of the oil obtained during the distillation of chips 1" × 1/4" × 1/8" at atmospheric, at 20 pounds, and then at 40 pounds pressure. During the first of the run at atmospheric pressure the gravity gradually increased, but never quite reached that of pure pine oil. By a continuous distillation at atmospheric pressure only about 50.5

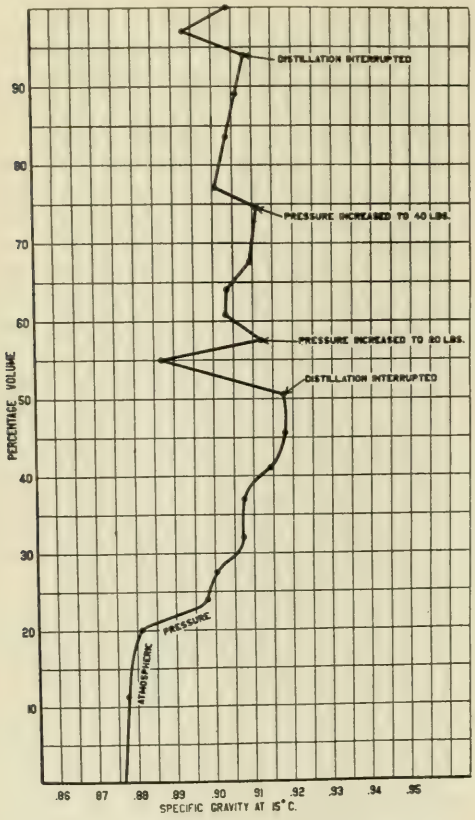

FIG. 7.—Curve showing fractionation of oil during Run 7.

per cent. of the total oil could be removed, but on interrupting the distillation for about fourteen hours and continuing again at atmospheric pressure, 7 per cent. more oil was obtained, the gravity of the first part of this 7 per cent. being much lower and of the last part only slightly lower than that of the last fraction of the continuous run. On increasing the pressure to 20 pounds, about 16.8 per cent. more oil was obtained, the gravity suddenly dropping and then gradually rising during the distillation of this 16.8 per cent. On increasing the pressure to 40 pounds and distilling continuously, a further yield of 19.5 per cent. was obtained, the gravity of this 19.5 per cent. dropping suddenly at first and then gradually rising. A similar additional yield was obtained by another interruption of the distillation, about 6 per cent. more oil being obtained.

Here again the effect of interrupting the distillation and of increasing the pressure are very plainly shown, *viz.*, increased yield of oil with gravity lower than the last fraction obtained before the conditions were changed.

This effect of the increased pressure in increasing the yields is due then to bringing more steam and oil into contact with each other than is possible at lower pressures. This could result either from a penetration of the steam further into the wood at the higher pressures or from a flow of resin toward the surface of the wood due to the decreased viscosity at the higher temperatures. It seems probable that both these have some influence, but the effect of the latter is quite certain, since it was noticeable that in the distillations made at high pressures a considerable amount of rosin would collect in the bottom of the retort or the outside of many of the chips would be coated with thin layers of rosin.

The effect due to the interruption of the distillation and continuing it again under the same conditions cannot be explained so readily, but it is probably due to a slow flow of rosin toward the surface or to the diffusion of the volatile oils in the rosin from the interior of the chip to the rosin at the surface from which the oil has been removed.

Application of Results.

The foregoing discussions have considered the effects of the different variables (1) size of chip, (2) pressure of steam, (3) speed of distillation, and (4) end point at which distillation is stopped, on (*a*) the yield of total oil, (*b*) the composition of the oil, and (*c*) the amount of steam required to remove the oil. It can be seen that there should be a certain combination of values for these variables which would give a most economical method of operation for a steam distillation plant; but there are other factors which must be taken into consideration in determining the proper combination of values. For instance, the best size of the chip will not be determined entirely by the effect of size on yield and efficiency, but also by the relative costs of preparing different-sized chips and the use to which the chips are to be put after steaming; the best pressure of steam will not be determined entirely by the effect of pressure on yield and efficiency, but also by the relative costs of high and low pressure steam and of apparatus designed for use with different pressures; the best speed for the distillation will not depend entirely upon the effect of speed on the yield of products and on the amount of steam required, but also upon the cost of steam and the overhead charges; the best end point at which to stop the distillation will not depend entirely upon the effect of end point on yield and efficiency, but also upon the cost of the raw material, the value of the products, etc.

Sufficient experimental data have been given, however, so that a knowledge of the various cost factors mentioned above (which would naturally vary a great deal in different plants) would make it possible to decide readily on the most economical methods for operating.

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THE DETERMINATION OF OXYGEN IN IRON AND STEEL BY REDUCTION IN AN ELECTRIC VACUUM FURNACE.[1]

By Wm. H. Walker and Walter A. Patrick.

At the fifth meeting of this Congress, held in Berlin in 1903, F. Lurman presented a paper on the determination of oxygen in iron and steel in which he pointed out the necessity of a new method which would measure the total oxygen in the sample, and especially that portion which is combined with manganese, aluminium, silicon, and the other oxides not reducible with hydrogen. Since that time no advance has been made in this important field of metallurgical work.

The important role which the oxides of iron and the other metals play in determining the physical and chemical properties of iron and steel was first clearly brought out by Prof. Ledebur in 1882. At this time Ledebur proposed the analytical method for determining oxygen which bears his name and which is based upon the reduction of the oxide at a red heat by hydrogen, and weighing the water thus formed. Owing to the fact that at a high temperature hydrogen reduces only the oxides of iron, leaving unattacked to a large extent the oxides of manganese, aluminium, silicon, titanium, etc., it is obvious that the method is not a satisfactory one, although up to the present the only one available for the purpose.

Other methods have been proposed for determining the oxygen in iron and steel based upon the solution of the constituents not oxides. As examples, may be mentioned the method of dissolving the sample in ethereal solutions of iodine and bromine; or that based upon the volatilization of the iron in a stream of chlorine gas at a high temperature; but none of these methods have proven of any value.

Although the detrimental effect of combined oxygen in iron and steel has been known since the time of Ledebur's first paper, it is only within the last few years that the full significance of these effects has been appreciated. That iron oxide can exist in iron and steel in more than one form seems certain, and that the oxides of the different metals associated with the iron should have characteristic effects is surely to be expected. But in the absence of any satisfactory analytical method for determining the oxide present, the relation between cause and effect has been of necessity a most imperfect one. It is hoped that the method of determining oxygen now to be described will be an aid in establishing the connection between the oxygen content and the physical and chemical properties of iron and steel.

In the now well known reaction wherein the oxides of the elements are converted into the corresponding carbides by heating them with an excess of carbon to a high temperature in an electric furnace, the oxygen is given off quantitatively as carbon monoxide. The quantitative formation of carbon monoxide is aided by an excess of carbon at high temperatures, and by a low pressure; also, as has been pointed out by Moissan, the refractory oxides are more readily reduced in the presence of metallic iron.

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

The details of the method as at present worked out are as follows:

A vacuum furnace of the Arsem type as supplied by the General Electric Co. is employed, and is shown in Fig. 1. The gun metal chamber *A* of the furnace of 20 cu. in. capacity rests inside the water

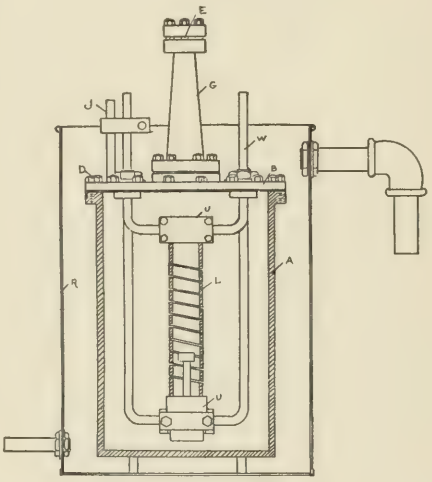

Fig. 1.

jacket *R*. The cover *B* is fastened to the chamber by means of 18 cap screws, *D*, and the joint is made tight by a rigid lead gasket. The tube *J*, through which the air is exhausted, is soldered into the cover. The window tube *G* is fastened to the cover by six cap screws, the joint made tight by another lead washer. The mica window *E* is placed in the top of the window tube. Current is led in through the electrodes *W*, which are brass tubes containing running water. The graphite heater *L* is fastened to the electrodes by means of the clamps *U*. The crucible is supported by the stand as shown in the figure and is thus placed in the hottest part of the furnace.

Twenty to twenty-five grams of the sample of metal in which the oxygen is to be determined are placed in a small graphite crucible and about four or five grams of finely powdered graphite added. The crucible is then placed in the furnace, the cover bolted down, and by means of a small rotary oil pump operated in series with a Geryk pump a vacuum of 0.01 of a mm. is obtained in the furnace in less than fifteen minutes. After thoroughly exhausting the furnace, the cooling water is turned on and the crucible and contents heated to about 500°–600° with the pump still running. This is necessary in order to pull away as completely as possible the oxygen absorbed by the heater and crucible. As carbon does not begin to reduce the oxides below 900° there is no danger in heating the crucible up to 500°. After fifteen minutes the furnace is allowed to cool, which it does very rapidly. Nitrogen that has been dried over sulphuric acid and phosphorus pentoxide is now allowed to enter the furnace until the latter is about half full. This is then pumped out and the crucible

again gently heated. Only by such a treatment is it possible to reduce the oxygen left in the furnace to a reasonably small value. It seems impossible to pump the absorbed oxygen entirely out of the furnace, but by washing with dry nitrogen it can be almost eliminated.

The stopcock leading to the pump is now turned off and seventy volts applied to the electrodes which causes a current of about 200 amperes to flow through the heater. A high temperature is reached very rapidly, the metal melting in three or four minutes. Just as the metal melts, violent ebullition very often occurs. This is prevented by opening the circuit for a short time and allowing the charge to cool. The metal soon becomes quiet and the heating is continued for twenty minutes. The furnace is then allowed to cool thoroughly, after which fresh air, or better nitrogen, that has been dried over sulphuric acid and phosphorus pentoxide is allowed to completely fill the furnace.

The gas now in the furnace is analyzed for carbon monoxide in the following manner:

The vessel *C* in Fig. 2 is exhausted by means of a

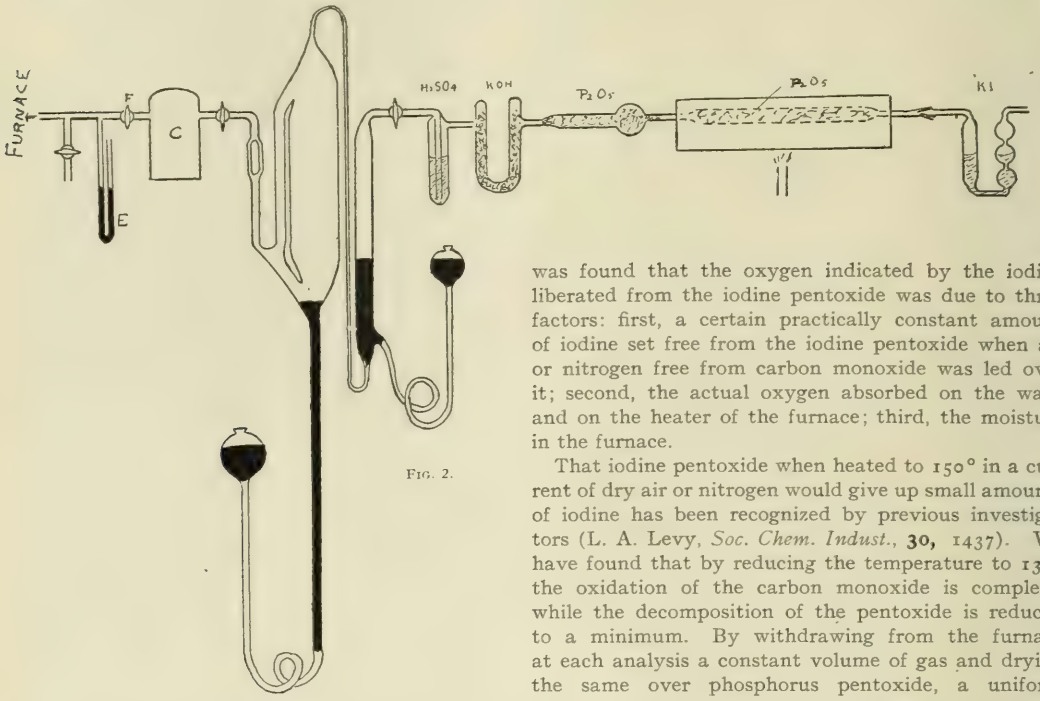

Fig. 2.

Toepler pump, and connections made with the furnace as shown in the diagram. The stopcock from the furnace is opened and if the gas in the furnace is under a pressure other than atmospheric, the difference is shown by the differential gage *E*. Correcting the barometric pressure by this amount gives the pressure of the gas inside the furnace. Stopcock *F* is now opened and the vessel and the pump filled with gas. A decrease in pressure corresponding to the volume of gas taken from the furnace is shown by the gage *E*, and we are thus able to calculate the fraction of gas taken from the furnace. By this method we are practically free from any errors due to temperature variation.

The gas is now slowly forced over iodine pentoxide which is heated to 130° C. and here the carbon monoxide is oxidized to carbon dioxide, liberating an equivalent amount of iodine. The latter is absorbed in a 10 per cent. solution of potassium iodine and subsequently titrated with $N/100$ sodium thiosulphate.[1]

A much more simple method of withdrawing an aliquot part of the gas for analysis, if a large quantity of mercury is available, is to use a mercury aspirator instead of the Toepler pump. By replacing the reservoir *C* by a liter bottle which may be filled with mercury, a known fraction of the contents of the furnace may be withdrawn, and forced directly through the iodine pentoxide tube.

The first point to be definitely determined was, how free from oxygen can the furnace and its heating element be made; in other words, using a sample of iron known to be free from oxygen, what amount of oxygen will be shown in a blank experiment? It was found that the oxygen indicated by the iodine liberated from the iodine pentoxide was due to three factors: first, a certain practically constant amount of iodine set free from the iodine pentoxide when air or nitrogen free from carbon monoxide was led over it; second, the actual oxygen absorbed on the walls and on the heater of the furnace; third, the moisture in the furnace.

That iodine pentoxide when heated to 150° in a current of dry air or nitrogen would give up small amounts of iodine has been recognized by previous investigators (L. A. Levy, *Soc. Chem. Indust.*, **30**, 1437). We have found that by reducing the temperature to 130° the oxidation of the carbon monoxide is complete, while the decomposition of the pentoxide is reduced to a minimum. By withdrawing from the furnace at each analysis a constant volume of gas and drying the same over phosphorus pentoxide, a uniform blank amounting to 0.006 gram oxygen for the furnace contents was obtained. The weight of oxygen absorbed on the walls of the furnace and in the heater when a vacuum of 0.01 mm. was maintained was found in blank analysis using iron free from oxygen to be 0.02 gram. If the air used to dilute the furnace contents previous to withdrawing the sample of gas for the carbon monoxide determination be not dried over phosphorus pentoxide, the amount of oxygen

[1] Nicloux and Gautier, *Compt. rend.*, **126**, 746; Kinnicut and Sanford, *J. Am. Chem. Soc.*, **22**, 14.

indicated may rise to 0.035 gram. By first exhausting the air from the furnace, and then filling with nitrogen and re-exhausting the amount of oxygen shown by a blank, analysis was found to be between 0.0120 and 0.0129 gram.

The accuracy of the method, so far as the ability to carry out the operations without introducing errors not corrected for as above, was shown by the fact that a sample of iron or steel containing oxygen may be heated, and the oxygen determined; upon reheating the same charge with additional carbon no further formation of carbon monoxide is obtained.

To determine the accuracy with which the oxygen of a sample of iron or steel will be converted to carbon monoxide, a number of analyses were made using an iron of very low oxygen content, and adding known quantities of the various oxides in the pure form. In addition to iron oxide, only the very refractory oxides of aluminium and silicon were used; other easily reducible oxides such as manganese and copper will introduce no difficulties. The weighed amount of the pure oxide together with a known weight of iron was placed in the graphite crucible and covered with powdered graphite and heated as described. From the oxygen as determined was subtracted that due to the blank and the iron and the following results were obtained:

	Weight of oxide.	Oxygen calculated.	Oxygen found.
Ferric oxide	0.5650	0.1695	0.1700
Ferric oxide	0.6525	0.1960	0.1940
Ferric oxide	0.8400	0.2520	0.2440
Ferric oxide	0.1516	0.0455	0.0480
Aluminium oxide	0.4925	0.2310	0.2040
Aluminium oxide	0.1860	0.0875	0.0810
Aluminium oxide	0.3065	0.1440	0.1260
Silica	0.0673	0.0360	0.0342
Silica	0.0320	0.0181	0.0171

While the results as obtained are not so accurate as is desired, the reduction being somewhat incomplete, and therefore the results uniformly low, the method has served to explain the discrepancies noted between the oxygen content as determined by the Ledebur method in certain samples and their physical and chemical properties. As examples of such analyses may be mentioned the following:

Sample No. 1 is a special heat of an open hearth steel to which iron ore and an excess of manganese was added in the ladle. The finished steel gave every evidence of having a high oxygen content, although, by the Ledebur method, but 0.006 per cent. oxygen was obtained. When determined by the vacuum furnace reduction method the real oxygen content of the steel proved to be 0.20 per cent.

Sample No. 2 is a high grade of open hearth steel in which the Ledebur method detected no oxygen. The vacuum method showed that there was 0.09 per cent. present.

No. 3, open hearth steel.

No. 4, same as No. 3 but from ingot to which ore was added.

Samples No. 5 and 6 represent two ingots from the same heat of open hearth steel of high quality. To No. 5 was added some iron oxide as the ingot was poured. The oxygen content of the ingot giving satisfactory results was 0.065 per cent. while that to which the ore was added and which was highly unsatisfactory proved to be 0.31 per cent.

No. 7, open hearth steel.

No. 8, open hearth steel.

No. 9, open hearth iron.

No. 10, open hearth iron.

Nos. 11*a* and 11*b* are duplicate analyses of an ingot iron of early manufacture. The vacuum furnace method indicates about three times as much oxygen as the Ledebur method.

Nos. 12*a* and 12*b* are ingot iron of later make and show an oxygen content of but 0.10 per cent. The full analyses are given in the following table:

No.	C.	Mn.	S.	P.	Si.	Cu.	O. Ledebur.	O. Vacuum furnace.
1	0.19	0.92	0.052	0.123	..	..	0.006	0.29
2	..	..	..	..	..	..	0.000	0.09
3	0.17	0.65	0.097	0.064	0.017	..	...	0.11
4	0.12	0.17	0.065	0.088	0.015	..	...	0.33
5	0.09	0.18	0.061	0.087	0.019	...	...	0.31
6	0.14	0.24	0.070	0.092	0.009	...	...	0.065
7	0.09	0.33	0.065	0.068	0.006	0.17	0.009	0.021
8	0.08	0.33	0.036	0.070	0.005	0.22	0.010	0.039
9	0.01	0.03	0.050	0.007	0.003	0.20	0.037	0.056
10	0.01	0.04	0.015	0.008	0.004	0.19	0.052	0.064
11*a*	0.01	trace	0.015	0.002	..	..	0.069	0.23
11*b*	0.01	trace	0.015	0.002	..	..	0.076	0.21
12*a*	0.02	0.03	0.029	0.004	0.0014	0.043	...	0.10
12*b*	0.02	0.03	0.029	0.004	0.0014	0.043	...	0.11

It is intended that this paper be considered a preliminary communication, and it is hoped that the method will be both simplified and improved by further work. It is published at this time in the hope that others interested in the effect of oxygen on steel will find in the idea something of value.

Massachusetts Institute of Technology,
Boston.

THE METHODS OF THE UNITED STATES STEEL CORPORATION FOR THE COMMERCIAL SAMPLING AND ANALYSIS OF PIG IRON.[1]

By the Chemists' Committee of the U. S. Steel Corporation.

PREFACE.

In conformity with the design of the officials of the United States Steel Corporation for the standardization of the methods employed in the sampling and analysis of all materials encountered in their various lines of manufacture, the Chemists' Committee presents this compilation of standard methods for the sampling and subsequent analysis of molten pig iron.

In selecting the methods, the committee employed the same line of procedure as in former cases, *viz.*, the careful consideration of all the methods employed in each laboratory of the corporation, evolving therefrom the several methods herein described, the immediate adoption of which is desired.

The services of Messrs. W. B. N. Hawk, Wm. Brady and C. H. Rich, a sub-committee appointed for the preparation of this pamphlet, are gratefully acknowledged.

INTRODUCTION.

A quite obvious cause of nonconformity of results of comparative analyses in the various laboratories of the Corporation has been an apparent lack of uniformity of method in the sampling and analysis of molten iron.

This condition is particularly apparent with regard to the determination of the sulphur, numerous discrepancies in which would appear to indicate the absence of, and the necessity for, some uniform method of procedure. The estimation of the sulphur by the gravimetric method and the determination of the remaining constituent elements of the iron, are susceptible of a most satisfactory degree of accuracy. The successful issue of the volumetric determination of the sulphur, however, is largely dependent upon

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York City, September, 1912. Copyright 1912 by J. M. Camp, Chairman Chemists' Committee, Munshall, Pa.

the grade of the iron and the conditions under which the test is taken. A disturbing factor in establishing a satisfactory standard of comparative values in such analyses is the loss of uncertain and varying proportions of the sulphur, due to the formation of volatile and difficultly oxidizable organic sulphides, upon solution of white or chilled iron in hydrochloric acid. Comparative tests by a number of chemists of the Corporation having shown quite satisfactory agreement in sulphur values as obtained by the evolution method in sand cast and properly taken so-called chilled test samples, it has been decided to adopt for all purposes the more convenient chilled test, which, it is believed, will tend to conserve the desired comparative accuracy. True values may be obtained in the crushed shot sample by annealing the powder in a current of natural gas or under any convenient non-oxidizing conditions, but the exigencies of the routine of the works laboratory, as demanded by the conditions necessarily involved in the manufacture of iron and steel, would, in most cases, prohibit this metallurgical refinement.

The methods of analysis herein described represent the best present-day practice and it is hoped that their adoption will go far toward reconciling those too often variant conditions, convenience of manipulation and accuracy of result.

The solutions as prescribed are indicated in their various proportions on a one-liter basis. It will be found convenient, however, in most cases to employ in actual practice corresponding multiples of a greater volume.

SAMPLING.

CHARACTER OF THE SAMPLE.—Two optional methods are prescribed for taking the test:

1. Plate or Pat Test.—With a suitable hand ladle a portion is dipped from the stream of molten iron and, with the spoon of the ladle resting upon a clean, dry, iron plate, a pat of such size as may be desired is poured thereon.

2. Chilled Mould Test.—With the spoon of the hand ladle resting upon the dry, clean mould (later to be described) a portion is poured sufficient to fill the mould.

The use of the water shot sample is to be considered as in violation of the standard method. The sand cast sample may be used but the uniform adoption of the pat or the chilled mould test is urged.

NUMBER OF SAMPLES TO BE TAKEN.—As tending to a reasonable degree of accuracy, it is recommended that a portion be secured, timed as nearly as may be practicable for the middle of each ladle of iron representing the cast. Equal portions from each of these samples are conveniently combined for the subsequent analysis.

PREPARATION OF THE SAMPLE.—The tests are either drilled or crushed as required. If crushed, only that portion passing an eighty-mesh sieve is used for the subsequent analysis.

DESCRIPTION OF THE MOULD.—Two convenient forms of mould are recommended, either of which may be used to advantage.

The mould (Fig. 1) furnishes a test which may be conveniently broken and crushed. The number of the furnace may be cast in the mould with Roman

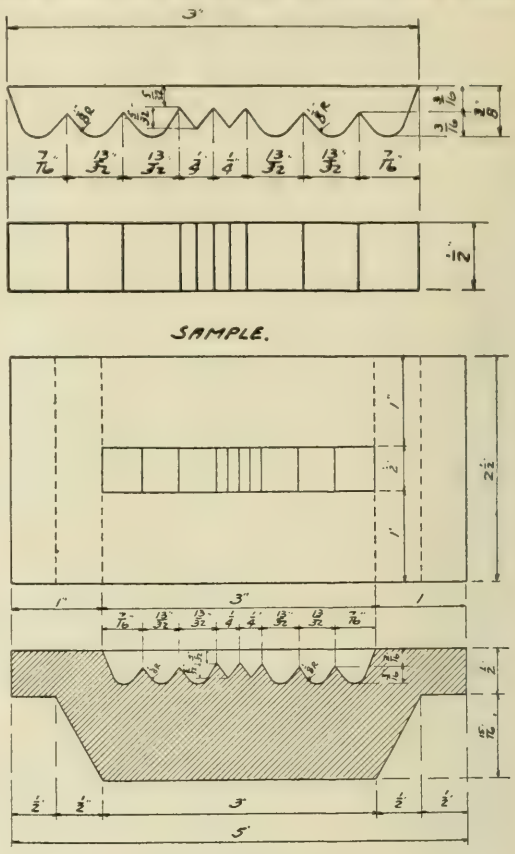

FIG. 1.—IRON MOULD AND TEST.

numerals or any other suitable form of designation. The two ridges shown in the test in this figure indicate that the test is taken from furnace No. 2.

The mould (Fig. 2) furnishes a test which may be either drilled or crushed. If the sample is to be crushed, the notched prolongation (T) is broken and crushed and the main body of the test reserved for the furnace man's fracture test. The furnace number may also be indicated in this form of mould in the same manner but not so conveniently and only in the main body of the test.

The moulds are made of cast iron and are illustrated in detail, with complete dimensions, in Figs. 1 and 2.

METHODS OF ANALYSIS.

DETERMINATION OF SILICON.

Drown's Method.—A single or double factor weight, 0.4693 or 0.9386 gram, of the sample is transferred to a glazed porcelain dish, 15–25 cc. of the silicon mixture added, gentle heat applied to the uncovered dish, and the solution evaporated to pronounced fumes of sulphuric anhydride. The dish is removed from the heat and allowed to cool, the residue

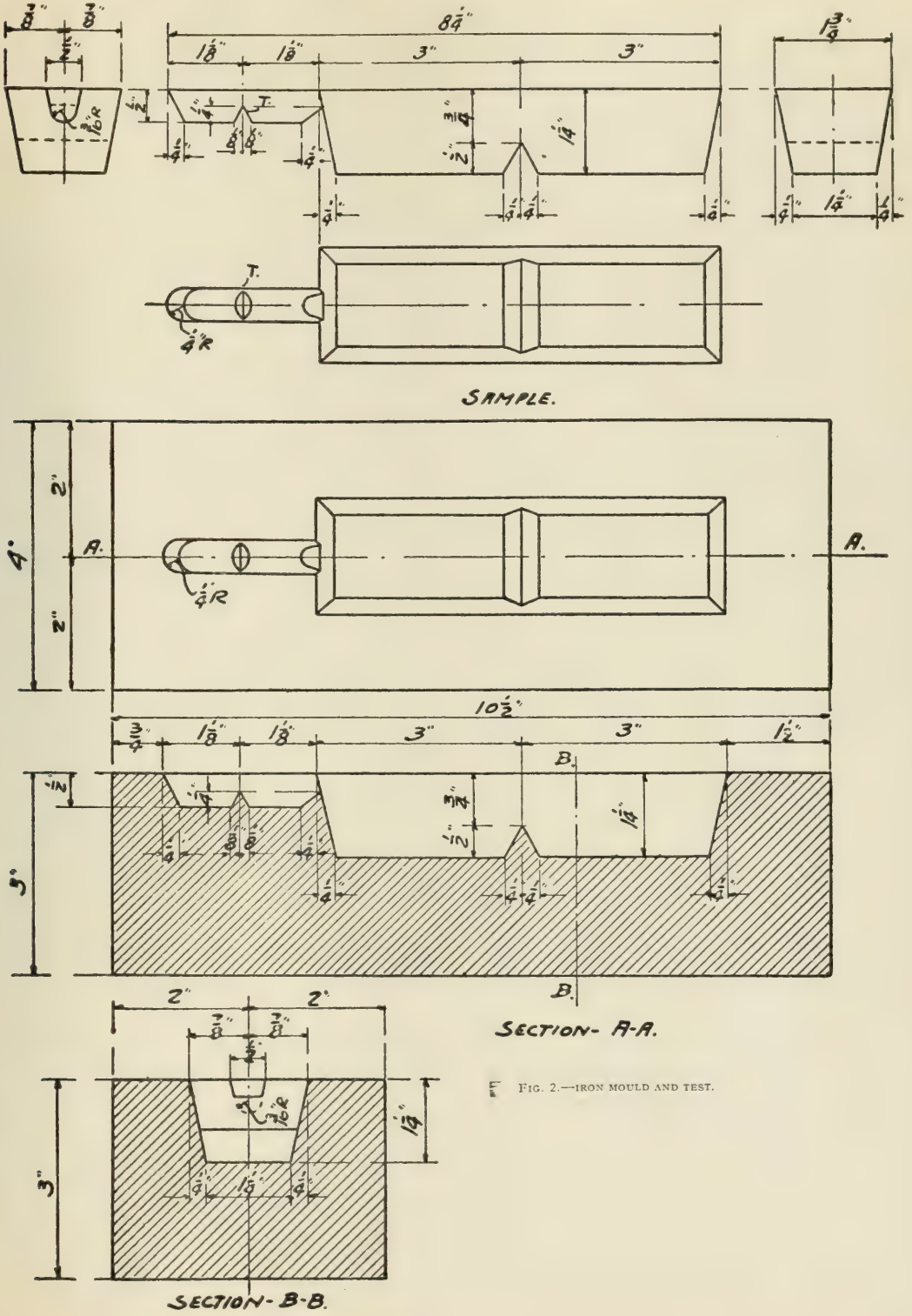

FIG. 2.—IRON MOULD AND TEST.

moistened with 10 cc. of the dilute hydrochloric acid, 50 cc. of hot water added and the solution heated without boiling until the soluble salts dissolve. The residue of silica and graphite is collected on a 9 cm. ashless filter, washed alternately with hot dilute hydrochloric acid and water to the disappearance of the soluble iron, and finally with hot water until free from chlorides. The residue is ignited uncovered in a weighed crucible at a moderate temperature until the carbon is completely oxidized, and finally for a few minutes at a higher temperature to the dehydration of the silica. The residual weight in milligrams divided by ten and corrected in conformity with the initial weight of the sample equals per cent. silicon.

Ford's Hydrochloric Acid Method.—This well known method is useful in point of rapidity, yielding satisfactory results in a shorter time than the more refined Drown's method. A single or double factor weight of the sample is transferred to a porcelain or platinum dish with cover glass, 20 or 30 cc. of concentrated hydrochloric acid added and the solution boiled rapidly to complete dryness; the residue is not baked. Ordinarily, decomposition is complete by the time the evaporation is effected. To the dry residue in the platinum dish there is added at once, or in the porcelain dish when sufficiently cooled, 20 cc. of the dilute hydrochloric acid. The solution is heated gently for a few minutes with the addition of 50–60 cc. water, and the heating continued until the soluble salts dissolve. The residue is collected and finally weighed as in the previously described Drown's method. The use of suction in the filtrations and the ignition of the residue in an atmosphere of oxygen will be appreciated as factors affecting the rapidity of the analyses in both of the above methods.

SOLUTIONS REQUIRED.

		Sp. gr.	Cc.
(1) *Silicon mixture*	nitric acid	1.20	750
	sulphuric acid	1.50	250
(2) *Dilute hydrochloric acid*	hydrochloric acid	1.20	500
	water		500

DETERMINATION OF SULPHUR.

Volumetric Method—Evolution Iodine Titration.—It is apparent that the evolution method is of comparative value only and is in no sense to be regarded as yielding the exact measure of the sulphur content of the iron, a fact of which due cognizance should be taken by all users of pig iron. Equally apparent, however, is the undoubted usefulness of the method in connection with the routine requirements of the iron laboratory and of the various metallurgical processes in conjunction with which it is used.

The apparatus as recommended for this determination consists of a flask of suitable form and size, preferably sixteen-ounce Florence ring neck with a two-hole rubber stopper equipped with an ordinary funnel or thistle tube and a short piece of glass tubing bent at right angles (exit tube) in the respective apertures. The exit or delivery tube is connected with the absorption vessel in such manner as to conduct the evolved gases to the bottom of the vessel. The absorption may be effected either in the beaker in which the titration is to be conducted, or in a test tube, preferably 10" by 1", suitably supported.

A minimum of 2.5 grams or a maximum of 5 grams of the sample is transferred to the flask, the stopper inserted and the flask conveniently connected with the vessel containing the absorbent; 40–60 cc. of dilute hydrochloric acid are introduced through the funnel and heat applied, a brisk evolution of the gases being maintained until the powder is decomposed. The temperature is then raised until the steam formed has forced the last trace of the hydrogen sulphide gas into the absorbent. The heat is removed, the apparatus disconnected and the titration conducted.

Ten cc. of the starch solution are added to the titrating beaker and the contents of the absorption tube transferred thereto. Both the absorption and delivery tube are rinsed with cold water and any adhering precipitate is dissolved by means of a fine jet of the dilute hydrochloric acid. Care is exercised that the acid solution be not unduly agitated before the introduction of the iodine solution. If the absorption is effected in the beaker, the delivery tube is removed first, cleansed with the acid and water and, with the precaution suggested above, an excess of the dilute acid is added. The final volume of the solution should approximate 400 cc. The solution is stirred gently in order to neutralize the alkali of the absorbent, which, if left undisturbed, reacts with the iodine with formation of a substitution product from which the iodine is but partially liberated upon acidifying the solution. The iodine solution is then added in successive portions, while the solution is stirred as the color fades, until the addition of a final drop yields the permanent blue color of the adopted end point. The number of cc. of the iodine required multiplied by 0.01 is equivalent to per cent. sulphur.

The volume of the solution in the absorption vessel is so adjusted as to insure a sufficient body for the absorption of all the gas, and a sufficient excess of the stock absorbent is maintained in proportion to the total volume of the solution. The proportions as used in the 10 in. by 1 in. test tube (15 cc. of any of the stock absorbents diluted to 60 cc.) may be taken as a basis therefor. If desired, the starch indicator solution may be added to any of the stock absorbent solutions in such proportions as to furnish the equivalent of 10 cc. of the indicator in the titration.

SOLUTIONS REQUIRED.

(1) *Starch Indicator.*—To one liter of boiling water in a suitable flask, a cold emulsion of six grams of starch suspended in 100 cc. of cold water is cautiously added, and the boiling continued five minutes after the final addition. The solution is cooled to room temperature, and, with the addition of six grams of zinc chloride in 50 cc. of cold water, mixed thoroughly and set aside for a day or two with occasional shaking. After the final subsidence of the heavier residue, the starch solution is siphoned into the container and the settings rejected. The zinc chloride is added as a preservative. Preliminary boiling of the water tends to lessen the frothing or formation of large bubbles on the addition of the starch.

(2) *Standard Iodine.*—Ten grams of potassium iodide crystals, followed by 4.5 grams of resublimed iodine, are transferred to a glass-stoppered graduated flask; 25 cc. of cold water are added and the flask is shaken until the iodine is completely dissolved. The solution is diluted to volume of one liter and set aside for not less than twenty-four hours before standardizing. The known sulphur of a standard steel, as determined both by the evolution and oxidation methods, is used as the basis of standardization with final adjustment so that 1 cc. is equivalent to 0.01 per cent. sulphur on the basis of the weight of sample used.

(3) *Dilute Hydrochloric Acid:*

Concentrated acid	500 cc.
Water	500 cc.

ABSORBENTS.

Ammoniacal Solution of Cadmium Chloride:

Cadmium chloride	5 grams
Water	375 cc.
Ammonia	625 cc.

Caustic Alkali:

Caustic potash or soda	5 grams
Water	1000 cc.

Ammoniacal Solution of Zinc Sulphate:

Zinc sulphate	10 grams
Strong ammonia	625 cc.
Water	375 cc.

Gravimetric Method.—Five grams of the sample are transferred to a clean No. 4 beaker or twelve-ounce Erlenmeyer flask, and with the addition of 100 cc. of concentrated nitric acid, gentle heat applied until solution is complete. It is sometimes necessary to check a too violent action of the acid, which might result in loss of unoxidized sulphur, by placing the beaker or flask in cold water. The solution is boiled briskly to low bulk, and after cooling somewhat, 30 cc. of strong hydrochloric acid are added, the solution is again concentrated, and following the precautionary addition of one gram of pure sodium carbonate, transferred to a clean porcelain dish and evaporated to complete dryness and the residue baked a short time at a moderate temperature.

The dish is allowed to cool, 35 cc. of concentrated hydrochloric acid are added and heat is applied until the soluble salts dissolve; the solution is again evaporated to complete dryness and the residue baked as before. This procedure insures the elimination of the nitric acid. The dish is cooled, 35 cc. of concentrated hydrochloric acid are added and heat is applied until the soluble salts are again dissolved. The cover is removed, and with the dish placed upon a suitable asbestos ring in order to prevent the formation of a crust of the metallic salts upon the sides, the solution is evaporated to the first appearance of the separation of the chlorides, which are then dissolved by the addition of a few drops of concentrated hydrochloric acid; three drops should suffice. Cold water is added to volume of about 75 cc., the residue collected upon an 11 cm. filter and the filtrate received in a No. 2 beaker. The residue and filter are washed with the least possible amount of the hot dilute hydrochloric acid, alternated with cold water, to the disappearance of the iron stains and finally with hot water to volume of about 200 cc. To this cold solution 10 cc. of a ten per cent. solution of barium chloride are added and the solution is allowed to stand with occasional stirring not less than twelve hours.

When the precipitate of barium sulphate has subsided, it is collected upon a 9 cm. close ashless filter, washed with dilute hydrochloric acid (five per cent.) to the disappearance of the iron and finally with hot water until free from chlorides. The filter and residue are ignited uncovered in a weighed crucible at a moderate temperature to the disappearance of the carbon of the paper and finally at a somewhat increased temperature for ten minutes. The residual weight multiplied by 13.74 and divided by 5 equals per cent. sulphur. The filtrate is set aside until satisfied that no further precipitation ensues.

The carbonaceous siliceous residue of the original solution usually retains some sulphur and is ignited in platinum under cover of pure sodium carbonate and decomposed by fusion with further addition of the carbonate and two-tenths gram of niter; the subsequent hydrochloric acid solution is freed from its silica and added to the original filtrate, or examined separately for sulphur.

It is apparent that absolute purity of reagents and cleanliness of utensils and the final weighing of the barium sulphate effected under the most exact conditions are determining factors in the successful issue of analyses by this method.

DETERMINATION OF PHOSPHORUS.

VOLUMETRIC METHOD.

I. Acid Alkali Titration.—One to two grams of the sample are transferred to a flask, preferably twelve-ounce Erlenmeyer, 40 cc. of nitric acid (1.13 sp. gr.) added and heat applied until the sample is decomposed. The sides of the flask are washed down, one gram of ammonium persulphate is added and the solution boiled until the combined carbon is completely oxidized. The residue is caught on an 11 cm. filter and washed with dilute nitric acid (2 per cent.) and hot water to the disappearance of the soluble iron. The filtrate is heated to boiling in a suitable flask, a slight excess of a solution of potassium permanganate added and the boiling continued until the excess of the permanganate is decomposed. The resultant precipitate of manganese dioxide is reduced to its soluble nitrate by means of the chosen reducing agent and the boiling continued until the excess thereof is decomposed.

With the solution at a temperature of 80° C., 40–60 cc. of ammonium molybdate solution are introduced and the flask is shaken for five minutes. The precipitate quickly subsides and is at once collected upon a 9 cm. filter, washed with dilute nitric acid (2 per cent.) until free from iron, and then with solution of potassium nitrate (1 per cent.) to the removal of the last trace of free acid.

The titration may be conducted in a beaker or in the flask in which the precipitation was effected. Care is exercised in the latter case to wash the flask thoroughly with the neutral wash, as any acid present of course reacts with the standard alkali. The filter and precipitate are transferred to the beaker or flask and the standard alkali is added in excess sufficient to render easy the subsequent maceration of the filter, which is accomplished by breaking up with a clean glass rod, or, if in a flask, by shaking the flask closed by a clean rubber stopper. When the precipitate has dissolved and the paper is thoroughly disintegrated, the solution is diluted and three drops of the indicator are added. The standard acid is then added to the disappearance of the pink tint, the sides of the titrating vessel washed down with cold water and, with a final volume of about 150 cc., the standard alkali is added to the adopted pink end point. The number of cc. of

the alkali used in excess of the acid, multiplied by 0.01 or 0.02, is the equivalent of phosphorus in hundredths per cent.

SOLUTIONS REQUIRED.

(1) *Standard Caustic Soda.*—Six and six-tenths grams of pure sodium hydroxide are dissolved in 100 cc. of boiled water. The solution is freed from any carbonic acid introduced by the caustic alkali, by the addition of about 1 cc. of a standard solution of barium hydroxide with subsequent filtration, and the solution finally diluted to volume of one liter. If desired, a stock solution may be carried, a convenient aliquot portion of which is diluted for the working solution.

(2) *Standard Nitric Acid.*—Ten cc. of concentrated acid diluted to one liter. The acid and alkali solutions are standardized against the known phosphorus of a standard steel with final correction so that they are exactly agreeing and 1 cc. is equivalent to 0.01 per cent. phosphorus on the basis of two grams of the sample.

(3) *Ammonium Molybdate.*—To 65 grams of molybdic acid (85 per cent.) suspended in 142 cc. of cold water in a suitable flask, 143 cc. of strong ammonia are added and the flask is rotated until the molybdic acid is completely dissolved. The solution is cooled and added slowly to 715 cc. of nitric acid of 1.20 sp. gr. while the acid solution is vigorously stirred.

Molybdic acid is, at times, encountered which fails to yield a permanently clear solution of the ammonium molybdate; the addition of one or more drops of a 10 per cent. solution of ammonium phosphate assisted in clarifying the solution. The solution is allowed to stand over night, when it is filtered into the container, preferably through purified asbestos and with the aid of suction.

(4) *Phenolphthalein.*—One gram dissolved in one liter of ethyl alcohol.

(5) *Nitric Acid* (1.13 sp. gr.):

Nitric acid—concentrated	240 cc.
Water	760 cc.

(6) *Potassium Permanganate Oxidant.*—Twenty-five grams to one liter.

REDUCING AGENTS.

Ammonium Bisulphite.—Five per cent. solution.

Ferrous Sulphate:

Ferrous sulphate	50 grams
Water	1000 cc.

Potassium Nitrite:

Potassium nitrite	50 grams
Water	1000 cc.

Sugar.—Saturated solution.

II. Potassium Permanganate Titration.—The yellow precipitate as above obtained is washed with ammonium sulphate solution, or if desired, dilute sulphuric acid (2 per cent.) until free from iron and molybdenum salts. Dilute ammonia (1 part ammonia and 3 parts water) is poured over the precipitate and the filter washed with hot water, and the solution caught in a flask in which the precipitation was effected. The volume of the solution should not exceed 25 cc. Eight grams of granulated zinc, 20-mesh, followed by 75 cc. of dilute sulphuric acid are added and the solution is gently boiled until reduction is complete. The undissolved zinc is then collected upon a glass wool filter and both flask and filter are washed with cold water. To the cold filtrate, standard potassium permanganate solution is added until a slight permanent pink tint is obtained. The measure of the permanganate solution required multiplied by its value in terms of phosphorus and divided by the initial weight of the sample equals per cent. phosphorus.

SOLUTIONS REQUIRED.

(1) *Acid Ammonium Sulphate:*

Strong ammonia	15 cc.
Sulphuric acid (1 part acid to 1 part water)	502 cc.
Diluted to one liter.	

(2) *Standard Potassium Permanganate.*—Two grams potassium permanganate dissolved in one liter of water. One cc. equals approximately 0.0056 per cent. phosphorus on a one-gram basis. The known phosphorus of a standard steel is used as the basis of standardization.

GRAVIMETRIC METHOD.

I. Weighing as Ammonium Phosphomolybdate.—One to five grams of the sample are transferred to a No. 5 glazed porcelain dish with cover glass, 25–60 cc. of nitric acid (1.13 sp. gr.) are cautiously added, gentle heat is applied until the sample is completely decomposed, and the solution is then rapidly boiled to dryness. The temperature is raised gradually with final heating of the uncovered dish over the full flame of an Argand or Bunsen burner to the complete expulsion of the acid. After cooling sufficiently to avoid danger of breaking the dish, 30 cc. of concentrated hydrochloric acid are added, heat is applied until the soluble salts are dissolved, and the solution rapidly boiled to the first appearance of the separation of the chlorides. This evaporation is conducted with the same regard to the prevention of the formation of a crust upon the sides of the dish as in the previously described method for the determination of sulphur. The dish is removed from the heat, 10 cc. of strong nitric acid are added and heat is again applied for about one minute. Cold water is added to volume of about 60 cc., the solution stirred with a clean glass rod and filtered into a suitable flask; the residue, collected upon an 11 cm. filter, is washed with 2 per cent. nitric acid and hot water alternately until free from iron, which insures also the complete removal of the soluble phosphate.

When the iron contains titanium in amount sufficient to interfere with the precipitation of the phosphorus and an exact determination is required, the residue of silica and graphitic carbon is ignited in a platinum crucible, the silica volatilized with hydrofluoric acid in the presence of a few drops of sulphuric acid and the resultant residue ignited and fused with sodium carbonate. The melt is boiled with hot water until disintegrated, the insoluble titanate collected upon a filter and the soluble phosphate added to the main solution.

To the clear filtrate with a volume of about 150 cc., 25 cc. of strong ammonia are added at once and the flask is shaken until the resultant precipitate has coagulated. The addition now of 25 cc. of strong nitric acid renders the solution clear and furnishes an excess of about 10 cc. of strong nitric acid—which, it is found, yields a pure crystalline precipitate of the phosphomolybdate with no tendency to creep. The relatively large amounts of ammonia and nitric acid added are prescribed in the case of 5-gram samples and are essential in that they insure a sufficient proportion of ammonium nitrate in the solution. It is evident that these additions may be decreased with smaller initial weights of the sample, but it will be found advantageous to maintain approximately the excess of 10 cc. of the nitric acid.

With the solution at a temperature of 80° C., 50–75 cc. of the molybdate solution are introduced and the solution agitated for about five minutes. When the yellow precipitate has finally subsided, it is collected upon a previously dried and weighed 9 cm. filter, the filter and contents are washed thoroughly with 2 per cent. nitric acid, dried for one hour in an air bath at a temperature of about 115° C. and weighed between watch glasses with ground edges and enclosed

in a suitable clip. It is of course essential that the light weight of the previously dried paper shall have been obtained under the same conditions. The increase in weight multiplied by 1.63 and divided by the initial weight taken is equivalent to per cent. phosphorus.

II. Weighing as Magnesium Pyrophosphate.—The yellow precipitate as above obtained is dissolved on the filter with hot ammonium citrate solution and the filter thoroughly washed with hot water, and the solution retained in a No. 0 beaker. To this cold solution, 5–10 cc. of the magnesia mixture are added, the solution is well stirred and allowed to stand in the cold not less than three hours. The precipitate of magnesium phosphate is collected upon a 9 cm. close ashless filter, washed with dilute ammonia, ignited at a low temperature to the disappearance of the carbon of the filter and finally for ten minutes at the full temperature of the blast. The weight of the magnesium pyrophosphate multiplied by 27.87 and divided by the initial weight taken is equivalent to per cent. phosphorus.

SOLUTIONS REQUIRED.

(1) *Ammonium Citrate:*

Citric acid	50 grams
Strong ammonia	350 cc.
Water	650 cc.

(2) *Magnesia Mixture:*

Magnesium sulphate	84 grams
Ammonium chloride	250 grams
Water	665 cc.
Ammonia	335 cc.

(3) *Dilute Ammonia:*

Strong ammonia	200 cc.
Water	800 cc.

DETERMINATION OF MANGANESE.

I. Walters' Color Comparison Method.—Fifty to two hundred mg. of the sample are transferred to a suitable tube or flask, preferably an 8 inch by 1 inch test tube or a two ounce Erlenmeyer flask, 10 cc. of nitric acid (1.20 sp. gr.) added and heat applied in a water bath or on a hot plate until the sample is decomposed. About one-half gram of moist ammonium persulphate, or its equivalent solution, is added and the heating continued until the combined carbon is completely oxidized. If silica or graphitic carbon separate in amount sufficient to render it necessary, the solution is filtered into a similar vessel and the residue retained on a small filter. The filter and residue are washed with the minimum of water, or the 15 cc. of silver nitrate solution required for the subsequent oxidation. The silver nitrate is introduced either through the filter or into the unfiltered solution, one gram of moist persulphate added and the heating continued until the characteristic pink tint of the permanganic acid is well defined. The solution is cooled, transferred to the comparison tube and the color matched against a suitable standard which has been treated in exactly the same manner and with the same relative initial weight. The relative volume of the solution as required to match the color of the standard is equivalent to hundredths per cent. manganese.

II. Volumetric Method.—The solution of permanganic acid is transferred to a beaker or flask, and following the addition of 10 cc. of sodium chloride solution, the standard sodium arsenite is added to the definite end point of the disappearance of the pink tint. The volume of the solution should not exceed 75 cc. If the silver is not precipitated, the reaction of the persulphate with the silver nitrate renders the end point somewhat fleeting and recurring. If conducted without delay, however, the titration may be accomplished with perfect satisfaction. The end point in this case while not so permanent is perhaps somewhat sharper than in the presence of the chloride.

When desired, a greater initial weight of the sample may be taken, the solution thereof diluted to a definite volume, the graphite and silica allowed to subside and aliquot portions withdrawn with a pipette.

SOLUTIONS REQUIRED.

(1) *Sodium Chloride.*—Two and one-half grams sodium chloride to one liter of water.

(2) *Silver Nitrate.*—About 66.5 grams of silver nitrate are dissolved in one liter of water. Twenty cc. of this diluted to one liter affords a solution of which 15 cc. is equivalent to approximately 0.02 gram of silver nitrate.

(3) *Sodium Arsenite.*—A stock solution is prepared by dissolving 10 grams of C. P. arsenious acid in a boiling aqueous solution of sodium carbonate (30 grams dissolved in 250 cc. of water), with final dilution of the cold solution to volume of one liter. Sixty-two and one-half cc. of this solution are diluted to volume of one liter for the working solution of which each cc. is equivalent to approximately one-tenth per cent. manganese, with an initial weight of two-tenths gram of the sample. The known manganese of a standard steel or iron is used as the basis of standardization.

III. Ford's Gravimetric Method.—Five grams of the sample are transferred to a No. 5. glazed porcelain dish with cover glass, 75 cc. of nitric acid (1.20 sp. gr.) cautiously added and gentle heat applied until the sample is decomposed, and the solution then rapidly boiled to complete dryness. The residue is baked a short time at a moderate temperature. The dish is cooled, 35 cc. of strong hydrochloric acid are added and heat is applied until the soluble salts dissolve. Cold water is added to approximately 60 cc., the solution filtered into a No. 5 beaker and the residue caught on an 11 cm. filter and washed with the least amount necessary of hot dilute hydrochloric acid and cold water alternately, to the disappearance of the soluble metallic salts. The filtrate is boiled to low bulk, cooled, 50 cc. of strong nitric acid are added and the solution is again boiled down to low bulk. The evaporation is repeated with successive portions of nitric acid to the complete expulsion of the hydrochloric acid and with conversion of the chlorides to their corresponding nitrates; the evaporation at this point is carried to the first indication of the separation of the nitrates as observed in the formation of a small nucleus of scum floating on the surface of the solution. After the solution has cooled somewhat, 75 cc. of strong nitric acid are added and the solution is again brought to the boiling point. To the boiling solution, crystals of potassium chlorate (five grams will be found sufficient) are cautiously added in small portions from a glass spoon, and the solution is boiled for five minutes.

The solution is allowed to cool before filtering. Filtration is effected through the medium of an asbestos plug held in a carbon filtering tube. The asbestos is prepared for use by heating with aqua regia to remove soluble lime salts and the plug is washed with

strong nitric acid before using. The precipitated manganese dioxide on the filter is then washed with successive additions of strong nitric acid (free from nitrous fumes) to the practical elimination of the iron; the acid is added first to the beaker and transferred from thence to the filter. After the final washing, suction is continued until the plug is practically dry, when the rubber stopper carrying the filter is transferred to a clean flask. The filtering tube is filled with 1 per cent. solution of ammonium bisulphite and allowed to stand about one minute, suction is then applied, successive portions of the bisulphite solution being added until the last trace of manganese dioxide is dissolved; the soluble manganese salt is finally washed from the abestos filter with hot water. The solution is transferred to a No. 4 beaker or, if preferred, retained in the flask, 10 cc. of strong nitric acid are added and the excess of the bisulphite is decomposed by boiling. The manganese dioxide could be dissolved perhaps more conveniently by means of hot hydrochloric acid, but the use of the bisulphite solution obviates the possible danger of contamination by traces of soluble lime or magnesia, which in some grades of asbestos seem to be in evidence notwithstanding numerous successive treatments with the hot acid.

The solution is cooled somewhat and ammonia is added to the point of a faint permanent precipitate, followed by the addition of 15 cc. of a 20 per cent. solution of ammonium acetate. The solution is boiled two minutes, filtered in a No. 5 beaker and the precipitate of the basic acetate of iron collected on an 11 cm. filter. The beaker or flask and the filter are washed twice with hot water, the precipitate is dissolved with hot dilute nitric acid and the solution returned to the vessel in which the precipitation was effected. The filter is washed with hot water until free from iron and the basic acetate precipitation and subsequent filtration repeated.

To the combined filtrates 5 cc. of glacial acetic acid are added and the solution is again brought to the boiling point; the cover glass is removed, 10 cc. of a 10 per cent. solution of ammonium or sodium phosphate added, and with the solution still at the boiling point and with constant stirring, strong ammonia is added to the first appearance of an incipient opalescence. The stirring is continued until the opalescence has developed into the characteristic crystalline precipitate, at which point the addition of the ammonia is continued, drop by drop and with constant stirring, until the total of 25 cc. has been added.

The precipitate is filtered at once upon an 11 cm. ashless filter and washed with dilute ammonia water (2 per cent.) until free from soluble salts. The filter and residue are ignited in a weighed porcelain or alundum crucible at a low temperature until the paper is burned off, and finally at a somewhat higher but still moderate temperature for ten minutes.

$$\frac{\text{Residual weight} \times 28.69}{5} = \text{per cent. manganese.}$$

DETERMINATION OF TOTAL CARBON

Direct Combustion Method.—The direct combustion of the carbon of iron or steel and their various alloys is fast coming to supersede the more tedious wet method. Certain limitations of this most excellent method, however, are to be noted. The inherent difficulty of successfully burning particles of steel of too great mass is apparent. Certain samples of both iron and steel or their alloys have been encountered of such a character as to necessitate the intimate admixture therewith of a finely divided metallic oxide, or, in the case of certain irons, fine drillings of low-carbon steel to assist in the oxidation. The powder of the crushed test of white iron requires a somewhat longer time for complete combustion than the drillings from the test of gray iron but with proper care may be burned with perfect satisfaction. An essential requirement in the conditions of the method is the close control of the temperature which should approximate a constant of 1000° C. and should not fall below 960° C. A pyrometer couple will be found convenient in controlling the temperature.

The combustion is conducted preferably in a fused quartz tube in either an electric or suitable gas-fired furnace. A platinum tube may be used but is subject to damage from possible splashing of the oxidized metal and is, moreover, much more expensive than the quartz. The use of litharge or other volatile and easily reducible oxides is, of course, prohibited in the platinum tube. The quartz tube is 24 inches long by $^3/_4$ inch or $^7/_8$ inch inside diameter, free from seams and selected of uniform diameter. Platinized asbestos, which may be secured at either end by short plugs of platinum gauze, is inserted for a space of 5 or 6 inches in the tube immediately following the position to be occupied by the boat. The rubber stopper at the end of the tube may be protected by the insertion of a removable plug of asbestos conveniently enclosed in a thin roll of platinum gauze. Platinum, nickel, alundum, porcelain or clay boats may be used. The dimensions, 3 to $3^1/_2$ inches long, by $^1/_4$ inch deep, $^1/_2$ inch wide at the bottom, flaring to $^5/_8$ inch at the top, all inside measurements, will be found convenient. Suitable furnaces for either direct or alternating current, with transformers, rheostats, etc., to suit the individual requirements may be obtained of the trade.

The oxygen from the high pressure cylinder under control of the reducing valve is purified by passing through caustic potash solution of 1.27 sp. gr. contained in washing bottles, preferably two arranged in tandem. A glass tube of convenient form and size, filled with granulated zinc, may be connected to the exit end of the combustion tube to retain possible fumes of sulphuric anhydride formed in the combustion of high sulphur irons. When the potash absorbent is used, a calcium chloride drying tube preceding the bulb or bottle is necessary.

Factor weights may conveniently be used in the direct combustion as follows: For the potash absorption and weighing of the bulb, 0.2727 gram or 0.5454

gram, where each one-tenth mg. gain in weight of the bulb is equivalent to 0.01 per cent. of 0.005 per cent. carbon, respectively. For the barium hydrate absorption, with ignition of the barium carbonate, 0.304 gram or 0.608 gram, where each one-tenth mg. of the weight of barium carbonate is equivalent to 0.002 per cent. and 0.001 per cent. carbon, respectively. For the titration methods it is convenient to employ for the initial weight even gram multiples, preferably 250 mg. to 500 mg.

One-quarter or one-half gram or the suitable factor weight of the sample is transferred to the boat. The boat is partially filled with ignited alundum depressed in the center in the form of a V about one inch in length, and in which the sample is spread in a compact mass. This intimate contact of the particles of iron conserves the heat for the continuous combustion of the carbon. The weighed potash container or the Meyer bulb tube, to which has been added 80–100 cc. of the barium hydroxide solution or 50 cc. of the standard potash solution, is connected with the tube and the boat is carefully pushed to its position in the center of the heat zone. The stopper of the tube is replaced and, with all connections tight, the current of oxygen is started at a rate approximating a continuous bubbling, as observed in the purifying solutions. It is essential that the tube should have acquired the maximum temperature before the introduction of the boat, a condition which will naturally obtain in the case of a continuous routine of combustion.

The first indication of the oxidation is observed in the sudden decrease of the bubbling of the oxygen through the absorption vessel. As the rate decreases the flow of oxygen is somewhat accelerated until the conclusion of the oxidation process as indicated by the recurrence of the rapid flow through the exit; the flow of oxygen is then reduced to the normal rate which is maintained for ten minutes to insure the complete oxidation of all the carbon and the final absorption of the resultant carbon dioxide. The absorption vessel is disconnected, the current of oxygen discontinued and the analysis concluded by either weighing the potash bulb, titrating the standard solution of caustic potash, filtering, igniting and weighing the precipitated barium carbonate, or titrating the excess of the barium hydrate solution with a weak solution of hydrochloric acid and without preliminary filtration.

I. By Increase of the Weight of the Potash Bulb or Bottle.—The perfectly clean and dry bulb or bottle is at once weighed. The increase in weight as noted in connection with the initial weight of the sample is corrected to per cent. carbon.

The potash container is prepared for use by carefully introducing the required volume of the solution, connecting with the apparatus and passing a current of oxygen through the hot combustion tube to the complete displacement of the air in the container. The vessel is disconnected and at once weighed. The weight so obtained furnishes the light weight for the succeeding combustion.

II. Titration of the Caustic Alkali.—The absorption in this case is effected in a Meyer bulb tube containing 50 cc. of the potash solution, accurately measured. The contents of the tube are transferred to a flask, the tube is cleansed with freshly boiled water, three drops of the phenolphthalein solution are introduced and dilute hydrochloric acid (one part acid to one part water) carefully added until the color begins to fade. The more dilute standard acid is then added until the addition of one drop just discharges the pink tint. The excess alkali which has not entered into combination with the carbon dioxide has now been neutralized and the solution is ready for the actual titration. One drop of the methyl orange or methyl red solution is added and the standard acid added in successive portions until the addition of one drop causes the characteristic change from the yellow to the rose tint in the solution. The measure of the acid required for this titration minus the equivalent required in the blank titration and multiplied by the carbon value of the solution equals per cent. carbon.

If preferred, the titration may be conducted with the phenolphthalein indicator, the measure of the standard acid required to discharge the pink tint being deducted from the blank equivalent and calculated to per cent. carbon as above. This method, however, would not appear to offer any advantage over the other and obviously requires more of the standard acid.

The blank equivalent is established by passing the oxygen through the hot combustion tube and into the measured volume of the absorbent solution with final titration as outlined above. The carbon value of the acid solution is established by titration of the measured volume of the potash solution following the combustion of a standard steel. Additional confirmation may be had by titrating against a standard solution of sodium carbonate. The use of sodium oxalate in this connection is recommended

SOLUTIONS REQUIRED.

(*1*) *Standard Acid, One-sixth Normal.*—Fifteen cc. hydrochloric acid (1.20 sp. gr.) diluted to one liter.

(*2*) *Caustic Potash, One-sixth Normal.*—Nine and one-half grams diluted to one liter. This solution need not of necessity be absolutely one-sixth normal.

(*3*) *Phenolphthalein.*—One gram dissolved in one liter of ethyl alcohol.

(*4*) *Methyl Orange.*— One gram dissolved in one liter of water.

(*5*) *Methyl Red.*—One gram dissolved in one liter of ethyl alcohol.

III. Filtration and Ignition of the Barium Carbonate.—The bulb tube is detached from the train, the index finger of the left hand being simultaneously placed over the exit end in order to prevent the solution from flowing back in the tube. The solution is filtered through an 11 cm. ashless filter, the filter and precipitate are washed with freshly boiled water (six good washings will be found sufficient), ignited in a weighed platinum crucible at a moderate temperature to the disappearance of the carbon of the filter and finally at a good full heat for five minutes. The weight of the barium carbonate multiplied by 6.08 and divided by the weight taken, or with correction in agreement with the initial factor weight, is equivalent to per cent. carbon. The solution and precipitate are transferred to the filter either by way of the bulb entrance with control of the flow by the index finger upon the open exit end of the tube or by control with

the thumb placed over the bulb entrance with the solution poured through the exit end. The precipitate may be readily removed by shaking the tube after successive additions of the water. The washing is conducted as thoroughly and expeditiously as possible and care is exercised to avoid the passage of air unduly through the filter.

IV. Titration of the Excess Barium Hydroxide.—The bulb tube is detached as before, the solution and precipitate are transferred to a twelve-ounce Erlenmeyer flask, and the tube thoroughly washed with freshly boiled water. Three drops of the indicator solution are introduced and the standard hydrochloric acid is added in successive small portions, while the flask is shaken, to the disappearance of the pink tint. The agitation of the solution insures the recovery of any carbon dioxide liberated upon the addition of the acid. The equivalent of the acid required in a preliminary blank titration minus the measure required in the actual titration, multiplied by the factor of the solution as determined by frequent combustions of a standard steel and in agreement with the initial weight of the sample, is equivalent to per cent. carbon.

SOLUTIONS REQUIRED.

(*1*) *Standard Hydrochloric Acid.*—Eight cc. of strong hydrochloric acid diluted to one liter. Freshly boiled water should be used in making up the solution. One cc. of this solution is equivalent to approximately 0.05 per cent. carbon on a one-gram basis.

(*2*) *Barium Hydroxide.*—Twenty grams of barium hydroxide crystals are dissolved in one liter of hot freshly boiled water and the flask covered and set aside to cool. When the solution has reached the room temperature, it is filtered as rapidly as possible through a 25 cm. filter into the container. The solution is preferably withdrawn from the container by means of an overflow pipette in conjunction with a suitable guard tube filled with soda lime or caustic potash solution.

(*3*) *Phenolphthalein.*—One gram dissolved in one liter of ethyl alcohol.

Solution and Combustion Method.—The conditions involved in the operation of this method admit of the employment of a greater initial weight of sample than in the previously described Direct Combustion Method.

One gram, or if the barium hydroxide absorbent is to be used, a ten factor weight (0.608 gram) of the sample is transferred to a No. 2 beaker or four-ounce Erlenmeyer flask; 100 cc. of the solution of copper and ammonium chloride or the potassium salt are added and the covered beaker is placed on a suitable stirring machine or stirred by hand, at a temperature of 60–70° C. until in solution, or, if a flask is used, it is placed on a shaking machine or closed with a clean rubber stopper and shaken by hand until solution is complete.

The carbonaceous residue is collected upon a filter of purified ignited asbestos made up in a perforated platinum boat, Gooch crucible or other suitable form of holder. The residue is washed by decantation with dilute hydrochloric acid to the disappearance of color in the washings, then transferred to the filter and washed with cold water until the acid is completely removed. Preliminary drying of the residue is not essential in routine work, but where the refinement of accuracy is desired, it is recommended that the residue be dried in a hot air or steam bath at a temperature of 100°–105° C. The residue is ignited in a platinum or silica tube, combustion crucible or other form of apparatus and in an atmosphere of pure oxygen or air free from carbon dioxide. The apparatus and the subsequent treatment of this carbonaceous residue may conveniently conform to the description of the method by direct combustion, and the final measure of the carbon established by any of the several optional methods therein described.

SOLUTIONS REQUIRED.

(*1*) *Copper and Ammonium Chloride.*—Three hundred grams of the pure salt are dissolved in one liter of boiling water. After cooling, 60 cc. of strong hydrochloric acid are added and the solution is filtered through a purified asbestos plug into the container.

(*2*) *Copper and Potassium Chloride.*—One pound dissolved in one liter of water, as above, with subsequent similar treatment.

(*3*) *Caustic Potash* (1.27 sp. gr.).—Three hundred grams dissolved in one liter of water.

DETERMINATION OF GRAPHITIC CARBON.

One gram or the ten-factor weight (0.608 gram) is transferred to a No. 2 beaker or a four-ounce Erlenmeyer flask, 40 cc. of nitric acid (1.13 sp. gr.) are added and gentle heat is applied until solution is complete. The solution is then boiled for a few minutes, the residue is collected upon a suitable asbestos or paper filter, washed alternately with hot dilute hydrochloric acid and water until free from iron and finally with hot water until free from acid. If the filtration has been conducted through an asbestos filter, the residue may be washed with hot caustic potash solution (1.10 sp. gr.) to remove separated silica. If preferred, a few drops of hydrofluoric acid may be added to the acid solution to dissolve the silica which might otherwise interfere with the filtration.

The analysis may be concluded in either of the following optional ways:

I. The graphitic residue is collected upon a suitable filter, washed with dilute hydrochloric acid and water and ignited in the combustion apparatus, and the measure of the graphitic content established as in the case of total carbon. It will be found convenient in this case to use the ten-factor weight of the sample.

II. The filter and graphitic residue are placed in a crucible and dried to constant weight at a temperature of 110° C., then ignited until the graphitic carbon and the filter paper are completely oxidized and again weighed. The loss in weight minus the weight of the filter paper when used and multiplied by one hundred is equivalent to per cent. graphitic carbon on a 1-gram sample.

DETERMINATION OF COMBINED CARBON.

I. Indirect Method.—The per cent. graphitic carbon as found above subtracted from that of the total yields the measure of the combined carbon. If desired, a direct estimation of the combined carbon may be conducted by the color comparison method.

II. Color Comparison Method.—The relatively exact chemical characteristics and preliminary heat treatment of the test piece and standard are universally recognized as fundamental bases of accuracy in the determination of the combined carbon of iron or steel by the color comparison method. The universal and continued use of this most convenient method in the analysis of steel products attests its efficiency within the close limits of control possible of attainment in the preparation of the steel standards. The appli-

cation of the method to the determination of the combined carbon of the various grades of iron is much more limited, owing to the larger and varying content of manganese and sulphur, the principal disturbing chemical factors affecting the color of the solution to be compared. It is apparent, however, that with a judicious selection of standards and careful control of all factors involved, the color comparison method may be applied to the determination of the combined carbon content of iron with a quite reasonable degree of accuracy.

The method of procedure as recommended is as follows: One gram of the sample is transferred to a dry, clean beaker, flask or tube, as desired. In the presence of graphitic carbon, the use of a magnetized spatula or wire in weighing off the sample is, of course, prohibited. Thirty cc. of nitric acid (1.20 sp. gr.) are added and heat is applied until the sample is decomposed. Graphitic carbon and silica are removed by filtration, and the filtrate retained in a 100 cc. graduated flask or cylinder. The filter is washed with cold water to the disappearance of color; the solution is diluted to volume, thoroughly mixed, and 10 cc. withdrawn with a pipette and transferred to the comparison tube. The color is then compared with the color of the solution of a standard iron in a similar tube and which has been treated in exactly the same manner and with the same relative initial weight. The simple calculation involved in the relative volumes of the two solutions yields the per cent. carbon in the sample.

A convenient aliquot portion of the above solution may be employed for the determination of manganese by the persulphate color method.

DETERMINATION OF TITANIUM.

Five grams of the sample are transferred to a No. 5 glazed porcelain dish or to a No. 4 beaker, with cover glass; 50 cc. of strong hydrochloric acid are added and the sample is digested until completely decomposed. Practically all of the titanium is said to remain insoluble with the silica and graphitic carbon. The insoluble residue is collected upon an 11 cm. filter, washed a few times with hot water, ignited in a platinum crucible and the silica volatilized with hydrofluoric acid in the presence of a few drops of sulphuric acid. The residue is then carefully ignited to the complete expulsion of the hydrofluoric acid, which if retained prohibits the subsequent colorimetric determination of the titanium.

Should it be desired to determine the usually quite negligible amount of titanium in the filtrate from the insoluble residue, it is recovered as follows: The filtrate in a No. 5 beaker is diluted to 250 cc. and strong ammonia added to the first appearance of a precipitate which slowly dissolves upon stirring. Dilute ammonia (2 per cent.) is added to a faint permanent precipitate, which is then dissolved by the addition of 15 cc. of a 10 per cent. solution of hydrochloric acid. The precipitate thus formed should dissolve rather slowly following vigorous stirring of the solution. One hundred cc. or more of a 20 per cent. solution of sodium hyposulphite are added and the solution in the beaker is stirred until the iron is completely reduced and the free sulphur begins to separate. The solution is then boiled for ten minutes and the precipitated titanic acid allowed to subside and collected upon an 11 cm. filter. The filter and precipitate are washed free from soluble salts with dilute acetic acid (2 per cent.) and ignited in the crucible containing the ignited residue from the previously conducted volatilization.

The combined residues are fused with 4 grams of sodium carbonate, the melt is disintegrated by boiling with hot water, and the insoluble sodium titanate is collected upon a 9 cm. filter and washed with hot water containing a little sodium carbonate. Hot, dilute sulphuric acid is added to the crucible which is then heated until the titanate is completely dissolved. The filter is spread upon the bottom of a No. 2 beaker, the contents of the crucible transferred thereto, and the crucible washed thoroughly with hot water. The beaker is then heated until the titanium salt dissolves, when the paper is removed and its burden of titanium sulphate returned to the beaker by washing with hot water. The solution is then transferred to the color comparison tube or if necessary to a graduated flask and aliquot portions taken. Shreds of filter paper which may be observed in the solution are removed by filtration.

In the color comparison, 5 cc. of C. P. hydrogen peroxide are added to the solution in the comparison tube and the solution is diluted to a volume yielding a color convenient for the subsequent comparison. A color equivalent to 0.005 gram of titanium in 100 cc. of solution will be found convenient. Water acidified with dilute sulphuric acid (equal parts acid and water) is then added to the standard tube to a volume allowing of subsequent necessary increase, 5 cc. of the hydrogen peroxide is added and the standard titanium solution added from a graduated burette in successive small additions until the colors agree. The measure of the standard solution required multiplied by its value in terms of titanium and corrected to agreement with the initial volume and weight is equivalent to per cent. titanium. If the color of the solution yielded by a convenient weight of the sample is of insufficient depth for an accurate comparison, adjustment may be made as follows: A measured volume of the standard titanium solution, sufficient to furnish the required depth of color, is added to the solution being tested and the comparison conducted as above described. The volume of the standard solution required in the comparison minus the equivalent previously added to the test solution is calculated to per cent. titanium. The volume of the two solutions must, of course, be identical in the final comparison.

In preparing the standard titanium solution 1.05 grams of ignited C. P. titanic acid are fused with 10 grams of sodium carbonate. The melt is digested with 100 cc. of hot water to the complete solution of the soluble alkali which is then filtered from the insoluble titanate. The residue of sodium titanate is washed with hot water containing a little sodium

carbonate and dissolved from the filter with 100 cc. of dilute sulphuric acid (equal parts acid and water) and the solution diluted to 1 liter. The titanium equivalent of this solution is ascertained by igniting and weighing the precipitated titanic acid of an aliquot portion following a separation with sodium hyposulphite as previously described. The ignited salt will be found to contain approximately 95.6 per cent. titanic acid. One cc. of the solution in the above proportion will therefore contain 0.6 mg. of titanium.

A gravimetric determination of the titanium in the iron may be conducted in the same manner, but inasmuch as in the colorimetric method the titanic acid as separated need be only relatively free from contamination by occluded salts, it is apparent that the latter method may be used to advantage, especially where many such determinations are required.

DETERMINATION OF COPPER.

Gravimetric Method.—Five grams of the sample are transferred to a glazed porcelain dish, 65 cc. of nitric acid (1.20 sp. gr.) added and the covered dish is heated until solution is practically complete. Twenty-five cc. of dilute sulphuric acid (equal parts acid and water) are then added and the solution is evaporated to fumes of sulphuric anhydride. Ten cc. of the dilute sulphuric acid followed by 50 cc. of hot water are added, the residue is heated until in solution, and the solution is filtered into a No. 4 beaker and the filter washed with hot water. The filtrate is diluted to 300 cc., heated to boiling and, with the addition of 25 cc. of concentrated ammonium bisulphite solution, the boiling continued to the complete reduction of the iron. Thirty cc. of a 20 per cent. solution of sodium hyposulphite are then added and the boiling is continued for five minutes or until the precipitated copper sulphide has coagulated. The precipitate is collected upon an ashless 11 cm. filter, washed with dilute nitric acid (2 per cent.) and hot water, carefully ignited and weighed. The weight of the copper oxide as noted, multiplied by 16 (80 divided by 5), equals per cent. copper. Too great a temperature in the ignition causes the copper oxide to fuse on the crucible. As the copper oxide is somewhat hygroscopic, as are also some porcelain crucibles, less error is encountered by igniting in platinum.

The ignited copper oxide carries with it traces of contaminating iron. If it be desired to correct this usually negligible error, the impure oxide is dissolved in the crucible with 10 cc. of strong nitric acid, the solution transferred to a No. 2 beaker and diluted to 100 cc.; the iron is then removed by an ammonia precipitation. The precipitate so obtained is collected upon a 9 cm. filter, washed with hot water, ignited in the crucible in which the previous ignition was conducted and the weight of ferric oxide noted. This weight is deducted from the weight of the impure copper oxide and the correction applied.

Volumetric Method.—The nitric acid solution of the impure copper oxide in the No. 2 beaker obtained as above described, is rapidly evaporated to the removal of the bulk of the free acid, and the solution diluted with cold water to volume of 150 cc. Strong ammonia is then added from a burette until the addition of a final drop causes the permanent bluing of the solution, after which there is added by means of a pipette six drops of acetic acid. Ten cc. of a 40 per cent. solution of potassium iodide are added and the standard sodium hyposulphite solution is run in until the color of the liberated iodine has almost disappeared. Ten cc. of the starch solution are now added and the addition of the standard sodium hyposulphite solution is continued to the final disappearance of the blue. The number of cc. of the standard solution required multiplied by its value in terms of copper and divided by five equals per cent. copper in the sample.

The value of the standard hypo solution is determined by titration of a solution of pure copper or by titrating the solution of a steel of known copper content. The apparent large excess of the potassium iodide employed is because of its relation to the final end point in the titration, the sharpness thereof decreasing in proportion as the excess of the iodide is decreased; the presence of ammonium salts in the solution also tends to lessen the permanency of the end point, hence the necessity for the preliminary evaporation of the acid solution.

If necessary, the time required for the volumetric determination may be materially lessened by initial solution of the sample in 50 cc. of dilute sulphuric acid (one part acid to three parts water), and the evaporation to dryness and filtration from the siliceous residue omitted. The iron in this case not being oxidized, the boiling with the ammonium bisulphite is also omitted. The copper oxide so obtained is contaminated to a greater degree by occluded iron, which if it be present in the final titration is prejudicial to a satisfactory end point. Thisiron is, however, readily removed by filtration following the evaporation of the nitric acid solution previous to the addition of the ammonia. It is apparent, also, that following the nitric acid solution of the sample, the preliminary treatment with ammonium bisulphite in the gravimetric method may be dispensed with, as the reduction may be accomplished by the addition of a sufficient excess of the sodium hyposulphite solution at the time of the precipitation of the copper sulphide. The precipitate formed under such conditions, however, carries an unduly large burden of separated sulphur, the presence of which would appear undesirable.

SOLUTIONS REQUIRED.

(1) *Standard Sodium Hyposulphite.*—Eight grams to one liter. One cc. is equivalent to approximately 0.002 gram copper.

(2) *Starch Solution.*—See the solution used in the volumetric determination of sulphur.

THE SYNTHESIS OF HYDROCARBONS AT HIGH TEMPERATURES AND PRESSURES.[1]

By J. N. Pring and D. M. Fairlie.

A systematic study of a number of chemical reactions at high gaseous pressures, in a specially constructed electric furnace, was first carried out by Hutton and Petavel.[2] Such reactions were studied

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

[2] *Phil. Trans. London* (*A*), **207**, 428 (1908).

as the formation of calcium carbide, silicon carbide, the reduction of alumina by carbon, the fusion of silica, and the synthesis of oxides of nitrogen. Temperatures up to about 3000° C. were used and pressures up to 200 atmospheres.

The present paper deals with a detailed investigation which has been conducted by the authors, on the synthesis of hydrocarbons at high temperatures and pressures. The apparatus constructed for this work is a modified form of the pressure furnace used by Hutton and Petavel.

The investigation, which was carried out at temperatures and pressures which were carefully measured and controlled, was directed mainly to the determination of the quantities of methane which are in equilibrium with carbon and hydrogen at different temperatures. In this way it has been possible to obtain data which will correlate the values for the specific heats of hydrogen, methane, and different forms of carbon at high temperatures. The influence of temperature on the displacement of the equilibrium constant of a chemical reaction is a function of the heat change which accompanies the reaction at that particular temperature, while the heat of reaction itself changes with the temperature according to the specific heats of the substances taking part in the equilibrium.

The dependence of a chemical equilibrium on the various heat changes involved in the reaction has been pointed out by van't Hoff, and further developed by Nernst and Haber, but there are very few cases where sufficiently accurate data are available to verify the application of these formulas at high temperatures.

In all cases when substances in a condensed system interact chemically, the reaction proceeds until a certain equilibrium stage is reached, when further action ceases, though in many cases the equilibrium stage is so far developed in one direction that the reaction appears to be complete.

At low temperatures equilibrium values are often of very little importance, since under these conditions the rate of chemical reaction is usually so slow that the equilibrium value is never reached and does not come into question. At high temperatures, however, the conditions are usually quite different, the final equilibrium stage being more quickly reached, so that usually chemical changes do not complete themselves, but proceed to a certain stage, at which point the same proportion between the substances taking part and the products of the reaction is obtained from whichever side the equilibrium is approached. At low temperatures, many substances are in an unstable or "metastable" condition, though they undergo no apparent change on standing, but at high temperatures this is not possible, as the change into the stable form proceeds with a velocity which continually increases with the temperature.

The reactions which have been investigated in this work, *viz.*, the synthesis of hydrocarbons, involve a case of the interaction of a solid with a gas. In the case of each hydrocarbon a certain equilibrium stage is reached when the particular hydrocarbon bears a definite ratio to the quantity of hydrogen present. The quantity of carbon does not come into consideration in this equilibrium, since its active mass does not vary under different conditions.

As methane is an exothermic compound, it follows that the equilibrium amount decreases with increase of temperature. Below 1000°, carbon and hydrogen at atmospheric pressure unite so slowly, even when the former is in presence of a catalyst like platinum, that equilibrium in the yield of methane cannot be reached in any reasonable time.

The velocity is considerably increased at high pressures, but even in this case it was not found practicable to determine the equilibrium value with methane below about 1100°.

Above this temperature, this synthesis was measured by heating carbon in the form of a rod in presence of hydrogen. The heating was effected by the passage of an electric current through the rod, which was thus the only part of the apparatus to be heated. The containing walls of the steel vessel were cooled by water.

Since methane is stable in larger amounts the lower the temperature, it follows that the quantity of this hydrocarbon finally yielded will correspond to the equilibrium at the temperature of the heated carbon, since no decomposition could occur in passing to the colder regions of the apparatus. A large amount of work has been carried out by the present authors[1] on the synthesis of hydrocarbons at atmospheric pressure and it has been found that traces of ethylene are also formed at 1300° and above, but the quantity does not reach any considerable magnitude below 1500° (at 1400° the quantity in equilibrium at atmospheric pressure is about 0.005 per cent.).

The ethylene will react rapidly with the hydrogen in the cooler part of the vessel, giving methane, and thus gradually raising the quantity of the latter above the equilibrium value at the high temperature. However, in the short time necessary to produce equilibrium with methane in these experiments at high pressures it was calculated that this disturbance would not reach any appreciable magnitude when working below 1500°.

With regard to the synthesis of acetylene, it was found in the earlier work cited above that this first becomes noticeable (about 0.0001 per cent.) at 1650°, and the amount produced increases with the temperature, in accordance with the fact of its being an endothermic compound.

However, it has not been possible to determine the precise equilibrium values with acetylene on account of the non-uniform temperature of the interior of the reaction vessel, which causes decomposition of the gas produced at the high temperature of the carbon to take place in regions of lower temperature. Moreover, at temperatures where the quantity of acetylene attains any considerable magnitude, an ex-

[1] Pring and Hutton, *Trans. Chem. Soc. London*, **89**, 1591 (1906). Pring, *Ibid.*, **97**, 498 (1910). Pring and Fairlie, *Ibid.*, **99**, 1796 (1911); **101** 91 (1912).

act estimation of the methane equilibrium is no longer possible on account of the rapid polymerization of the acetylene with hydrogen, giving methane in the cooler parts of the vessel. For this reason, it has only been found possible in this work to measure with any accuracy the equilibrium with methane, and that only in the range of temperature between 1100° and 1600°, though the experiments were extended up to 2100°. It has been shown, moreover, that in this range, and at pressures up to 200 atmospheres, no hydrocarbons other than methane, ethylene, and acetylene can be formed or can exist in any detectable quantity.

Considering the synthesis of methane, since the equilibrium is expressed by the equation

$$C + 2H_2 = CH_4,$$

it follows in accordance with the law of mass action that $\frac{p\text{-}CH_4}{p\text{-}(H_2)^2} = K$ or the concentration of methane divided by the square of that of the hydrogen is a constant at any particular temperature. It follows from this that an increase in the pressure of n times will increase the ratio of methane to hydrogen n times.

A proof that definite equilibrium values are obtained lies in the fact of the same final quantity of methane resulting in whichever direction the reaction is made to proceed, and further by the same value being obtained for K, the equilibrium constant, whatever gaseous pressures were employed.

DESCRIPTION OF APPARATUS.

The pressure cylinder (V) (Fig. 1) was forged from a piece of nickel steel of high tensile strength. The steel tubes $E\,E$ which served to lead in the current were cooled by water circulation, and contact with the carbon was made by means of nickel clamps, $N\,N$, which were brazed to the ends of these leads. The arrangement in the diagram shows provision for heating wider carbon tubes in which crucibles can be placed, but for the present purpose, tubes or rods of carbon longer and narrower than the one shown in the diagram were used. These rods or tubes C were always fitted in graphite end pieces, which were held in the nickel clamps. The steel tubes emerged from the furnace at the stuffing boxes $P\,P$ and were insulated from the walls by means of small tubes of ebonite or fiber, $F\,F$. Asbestos cord mixed with a little tallow was used as the packing material for the boxes $P\,P$, and was compressed by the brass rings $R\,R$, which were forced down onto the ebonite tubes by 6 bolts, as at $K\,K$. The outward thrust of the electrodes was secured by the bolts $T\,T$, of which there were two at each end of the furnace. The top part of the furnace was fastened down by 6 bolts as at $B\,B$, and a gas-tight joint made by means of the lead spigot $S\,S$. By opening the bottom stuffing box and removing the packing, the bottom electrode could be lifted while clamped to the carbon rod which was also held in the top electrode. The two electrodes and the carbon tube could thus be all lowered into position together with the furnace top, and afterwards raised in the same manner. Water circulation was provided in the annular jacket M, the gas admitted through the valve V, and the pressure read directly on a gauge. The glass window W was placed

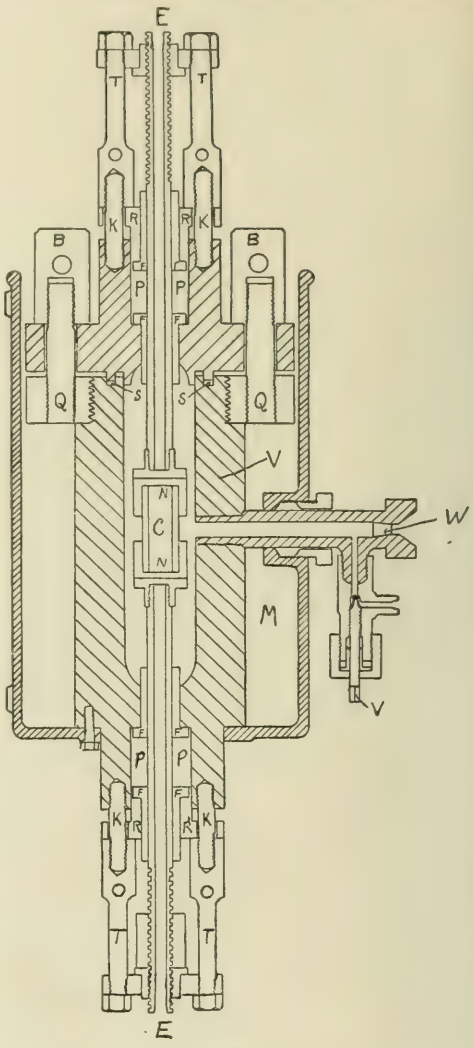

FIG. 1.

at a sufficient distance to be protected from the heat of the carbon. Temperature readings were taken by means of a Wanner optical pyrometer, from the light radiated from the carbon, after passing through the window and being reflected from a mirror placed in front at an angle of 45°. By comparing the optical readings in the case of graphite with those given at the same time by a thermojunction, it has been found that there was no appreciable departure at 1300°, so that graphite must radiate approximately like the theoretical "black body." Measurements were made from time to time of the error arising from the absorption of the window and mirror. At 1400°, this usually amounted to about 60°. The absorption at any

other temperature can be calculated from the formula $\frac{1}{T_1} = \frac{1}{T_2} - C$, where T_1 is the real, T_2 the apparent temperature after absorption, and C is a constant for any given sample of glass.[1]

The window could, as a rule, be safely used with pressures up to 200 atmospheres and the remainder of the furnace was capable of withstanding a pressure of 1000 atms.

The carbon used at C consisted in some cases of the amorphous retort variety in the form of tubes 12 cm. long and either 20 mm. external and 15 mm. internal, or 15 mm. external and 7 mm. internal diameter.

With the smaller size, a current of 500 amps. at 27 volts would raise the temperature to 1600°, when using hydrogen at 150 atmospheres pressure.

In other experiments, rods of graphite (Acheson) 12 cm. long and 9 mm. diameter were used.

In the case of amorphous carbon, when given no preliminary purification, after mounting in the furnace, a partial purification was obtained by heating to about 1400° in hydrogen at about 50 atmospheres pressure, and then liberating and renewing the gas.

The quantity of combined hydrogen present as impurity in the carbon was always well below the amount of methane subsequently synthesized. The capacity of the furnace was about 750 cc. A number of experiments at lower pressures were carried out with rods of amorphous carbon, 5 to 7 mm. diam. and 12 cm. long, which had been carefully purified by heating electrically in chlorine in a glass vessel to about 1500° for a few hours, and then in hydrogen in the same manner.

On account of the corrosion of the carbon, it was not as a rule possible to use the same rod or tube in more than one experiment. In the course of a large amount of work where carbon rods and tubes have been heated at atmospheric pressure under different conditions, it has been found that the heating, in the case of amorphous carbon, always takes place with great uniformity throughout the whole length and up to the cooled points of support. This is due to the negative temperature coefficient of resistance which causes a greater expenditure of electrical energy in places which tend to become cooler. With graphite, however, the temperature falls near the cold ends of support.

PREPARATION OF MATERIALS.

Hydrogen.—Electrolytic hydrogen was obtained commercially in steel bottles at a pressure of 120 atms. On analysis, it was found to contain 0.2 per cent. of nitrogen, and no appreciable quantity of other impurity. After admitting the gas to the furnace, the heating of the carbon enabled the pressure to be raised to 200 atmospheres.

Carbon.—Different varieties of carbon were used as explained above, and in some cases were first purified by heating to a high temperature in an atmosphere of chlorine.

In some experiments the carbon was used in presence of platinum or palladium, to act as a catalyst. For this purpose a layer of the metal was obtained by electrodeposition from a chloride solution.

Methane.—In some experiments an atmosphere of methane was admitted to the previously evacuated furnace, before filling in the hydrogen at high pressure. The hydrocarbon for this purpose was prepared by decomposing commercial aluminium carbide with water, washing the gas with ammoniacal cuprous chloride to remove acetylene and hydrogen sulphide, and then liquefying by means of liquid air. After evaporation, the gas was collected over water in a large holder of 20 liters capacity.

ANALYSIS OF GASES.

The gas obtained in these experiments, which contained from 1 to 20 per cent. methane was analyzed. in the Sodeau apparatus. By shaking the gas with an ammoniacal silver nitrate solution, acetylene (if present) was completely, and ethylene, partly absorbed. The remainder of the ethylene could then be removed by means of bromine. Carbon monoxide was then taken out by shaking with a freshly prepared solution of ammoniacal cuprous chloride. The hydrogen was then removed by mixing with an excess of oxygen and passing a few times over palladium sponge maintained at about 80° in a water bath.[1]

The saturated hydrocarbon could then be identified and estimated by the relation found between the contraction after combustion with oxygen, and the volume of carbon dioxide formed, as ascertained by absorption with potassium hydrate solution. In all these cases, methane was at all temperatures found to be the only saturated hydrocarbon produced.

In an experiment carried out at 1275°, an examination was made for traces of ethylene by circulating a large quantity of the gas (25 liters) through a tube cooled in liquid air. Most of the methane was thus condensed, together with practically the whole of any ethylene present, as the latter has a higher boiling point than methane. This liquid was then allowed to evaporate slowly, and the last portion was passed through a tube containing carefully purified cocoanut charcoal, which had previously been heated for some time at a red heat in a high vacuum. The gas absorbed by the charcoal in this experiment was then removed in fractions by evacuating. The last portion of 50 cc. was analyzed and found to contain 0.51 cc. of ethylene or 0.002 per cent. of the total gas, while the amount of methane in this particular sample was 21 per cent. The ratio of ethylene to methane is lower than that found in earlier work at atmospheric pressure, and the ratio of ethylene to hydrogen is higher. This result is in agreement with the effect which would be expected theoretically from the influence of pressure on the yield of the different hydrocarbons.

CHANGE OF PRESSURE.

The formation of methane, proceeding according to the equation

$$C + 2H_2 = CH_4,$$

is accompanied by a contraction of volume equiva-

[1] Pring, "Lab. Exercises in Phys. Chemistry," page 151. Manchester University Press.

[1] Compare Pring and Fairlie, *Trans. Chem. Soc. (London)*, **99**, 1796 (1911).

lent to the volume of methane formed. In these experiments at constant volume this was equivalent to a change of pressure.

Consequently by reading the pressure indicated by the gage, the course of the reaction could usually be followed, and the attainment of equilibrium recognized. However, a considerable time was usually necessary for the mean temperature of the enclosure to become constant on account of the large quantity of metal present. Samples of gas were usually withdrawn at two or more different periods during the experiment, in order to ascertain when equilibrium had been reached.

The results of all experiments which were completed are tabulated below according to the particular variety of carbon, and in order of temperature.

As follows from the unstable nature of amorphous carbon, it was found that this modification gradually changed into graphite during the experiments in which it was heated at temperatures above 1100°, in presence of hydrogen. This change took place more rapidly the higher the temperature. It was found that the amorphous carbon which had been purified by heating to a high temperature in chlorine and then in hydrogen was always more or less graphitized.

Amorphous carbon was found to give a considerably higher percentage of methane than graphite, and

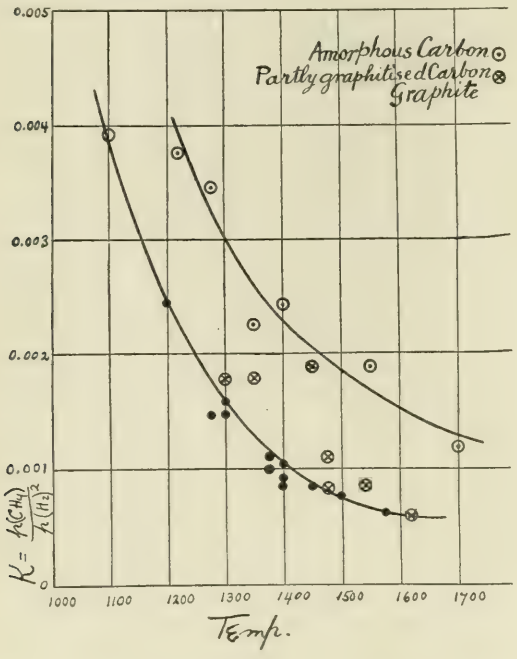

FIG. 2.

on beginning an experiment with amorphous carbon, the yield of methane which was at first obtained gradually fell concomitantly with the change of amorphous carbon into graphite. The increased yield of methane with amorphous carbon is in excess of the stable equilibrium value, and thus denotes a false or metastable equilibrium. This is possible only to such a degree on account of the great inertness of methane, or the slow rate at which it breaks down into carbon and hydrogen.

These false equilibrium values with amorphous carbon have also been noticed by Schenck and Heller,[1] who studied the equilibrium in some reactions in which carbon in different modifications takes part.

In the case of the equilibrium between carbon dioxide, carbon monoxide, and carbon, the reduction of the first was greatest when amorphous carbon was used.

A similar result was obtained in the reaction between iron oxide and carbon, thus in this case, at 550°, the pressure of the latter when in "metastable" equilibrium was, with amorphous carbon, 59 mm.; diamond, 22 mm.; and the stable equilibrium value with graphite was 12 mm.

In the present work the results with amorphous carbon are given in Table I below. In some cases the carbon was impure (though containing less total hydrogen than the quantity of methane subsequently formed); in others, the substance was partly purified in chlorine at a temperature too low to cause any appreciable change into graphite. In all cases the results in this table refer to carbon which was used for the first time. In Table II are given the experiments done with graphite. This was either Acheson graphite or else carbon which had been used in a previous experiment and heated for a long interval at a high temperature in hydrogen, or else it had been purified at a high temperature in chlorine so as to cause transformation into graphite. The carbon in all these cases was practically pure.

In Table III are given the experiments with carbon which by previous heating or purification had become partly transformed into graphite. In some cases a thin layer of platinum or palladium was coated onto the carbon by electrodeposition as explained above to serve as a catalyst. These cases are pointed out in the first column of the tables.

The whole of the results are entered in Fig. 2, though a number of the experiments in the case of graphite were not quite taken to the equilibrium point, so that the curve has been drawn through the maximum values.

The values obtained in experiments below about 1700° do not represent equilibrium quantities, as the methane in these cases is formed chiefly by the reaction of ethylene and acetylene with hydrogen in the cooler parts of the vessel. The results at these higher temperatures are consequently not plotted in the figure.

RESULTS AND CONCLUSIONS.

The reaction between carbon and hydrogen resulting in the formation of methane was found to proceed with increased velocity at high gaseous pressures. Using carbon in the form of a compact rod or tube, and either in presence or absence of a catalyst, the equilibrium stage was reached in about 2 hours, when the temperature was 1200° to 1300° C., and the pressure 30 to 50 atms. Above 1400° C., equilibrium was reached

[1] *Ber. d. chem. Ges.*, **38**, 2139 (1905).

TABLE I.—AMORPHOUS CARBON. FIRST TIME OF USE.

NATURE OF CARBON.	TEMPERATURE. CENTIGRADE.	TIME.	ATMOSPHERES PRESSURE.	PERCENTAGE COMPOSITION. CO.	CH_4.	C_2H_2.	C_2H_4.	$K = \frac{p\text{-}CH_4}{p\text{-}(H_2)^2}$
Purified, platinum-coated	1100°	0	...		4.10			
		2½ hrs.	20	1.1	6.35			0.00390
Impure, platinum-coated	1220°	0 hrs.	...	...	4.1			
		3 hrs.	18	1.4	5.6			0.00376
Partly purified	1275°	3 hrs.	100.0	0.25	21.5		0.002	0.00359
Impure, platinum-coated	1350°	1 hr.	166.0	0.6	18.5			0.00173
		2½ hrs.	153.0	0.7	20.9			0.00224
Purified, platinum-coated	1400°	0			4.35			
		1¾	18	0.92	3.86			0.00245
Same carbon as above:								
(To show effect of progressive graphitization)	1400°	1½ hrs.	19.0	1.0	2.35			0.00138
		3 hrs.	18.5	1.4	1.98			0.00120
		4½ hrs.	17.5	3.3	1.28			0.00084
Impure	1550°	0	...	...	4.65			
		1½ hrs.	21.0	1.5	3.49	...	...	0.00188
Impure	1620°	20 mins.	20.0	3.7	1.0	...		0.00058
" platinum-coated	1700°	1 hr.	15.0	7.5	1.4	nil		0.00120
"	1775°	4 hrs.	117.0	1.6	9.0	nil	0.1	...
"	1950°	7 mins.	24.5	3.4	2.4	0.29	0.44	...
"	2050°	7 mins.	23.0	2.8	2.8	0.74	1.10	...
Purified	2100°	0	...	...	5.5	...	...	...
		15 mins.	25.0	5.5	2.6	0.25	?	...

TABLE II.—NATURE OF GRAPHITE.

NATURE OF GRAPHITE.	TEMPERATURE. CENTIGRADE.	TIME.	ATMOSPHERES PRESSURE.	PERCENTAGE COMPOSITION OF GAS. CO.	CH_4.	$K = \frac{p\text{-}CH_4}{p\text{-}(H_2)^2}$
Acheson	1200°	2½ hrs.	105.0	0.0	17.5	0.00244
Carbon graphitized by heating, platinum-coated	1275°	0	...		2.38	...
		25 mins.	37.0	1.6	4.23	0.00133
		1¾ hrs.	32.0	2.4	4.02	0.00147
Carbon graphitized by heating, palladium coated	1300°	½ hr.	37.0	0.6	4.69	0.00120
		1 hr.	35.5	1.0	4.55	0.00146
Acheson	1300°	1 hr.	117.0	0.0	11.2	0.00126
		2¼ hrs.	106.0	0.0	12.6	0.00158
Carbon graphitized by heating	1375°	1 hr.	28.0	1.4	2.5	0.00100
Acheson	1375°	3 hrs.	115.0	0.2	10.6	0.00117
Graphitized by heating, palladium-coated	1400°	0	...	...	2.4	...
		¼ hr.	46.0	0.1	3.90	0.000945
		1¼ hrs.	46.0	0.2	4.29	0.00103
Graphitized by heating, platinum coated	1400°	0	...	...	1.6	...
		1½ hr	50.0	1.3	3.99	0.00089
Same carbon as above	1400°	0	...	...	1.6	...
		¾ hr.	55.0	0.5	4.24	0.00080
		1¾ hrs.	48.0	1.0	3.71	0.00089
Carbon graphitized by heating, platinum-coated	1450°	0	...	...	2.3	...
		20 mins.	47.0	2.0	3.39	0.000843
		1 hr.	44.0	2.4	3.01	0.000746
Carbon graphitized by heating, platinum-coated	1500°	0	...	...	1.8	...
		½ hr.	55.0	0.8	3.96	0.00080
		1 hr.	52.0	1.2	3.62	0.00077
Carbon graphitized by heating, platinum-coated	1575°	0	...	...	...	...
		12 mins.	52.0	0.7	2.94	0.00063
		1½ hrs.	44.0	1.0	2.46	0.00062

TABLE III.—PARTLY GRAPHITIZED CARBON.

NATURE OF CARBON.	TEMPERATURE. CENTIGRADE.	TIME.	ATMOSPHERES PRESSURE.	PERCENTAGE COMPOSITION OF GAS. CO.	CH_4.	$K = \frac{p\text{-}CH_4}{p\text{-}(H_2)^2}$
Purified	1300°	1¾ hrs.	7	7.3	1.0	0.00178
Impure, platinum-coated	1350°	2 hrs.	11.5	5.75	1.71	0.00178
Purified, "	1450°	1¼ hrs.	136	0.3	17.1	0.00186
Impure, " "	1475°	1¼ hrs.	177	0.3	16.7	0.00137
		4½ hrs.	155	0.3	11.9	0.00101
Impure	1475°	1¼ hrs.	200	0.05	13.1	0.00087
		3¼ hrs.	200	0.25	12.4	0.00083
Impure	1540°	1½ hrs.	183	0.05	12.0	0.000860

in about 15 minutes under the same conditions. At 200 atmospheres the reaction was still more rapid.

The results indicate the probability that carbon in a fine state of division would, at still higher pressures, combine with hydrogen with extreme rapidity, as the action is exothermic. In this way the preparation of methane, though necessarily present with a small percentage of hydrogen, might most conveniently be carried out on a large scale.

The relative amount of methane produced increases

with the pressure to the extent demanded by the law of mass action as applied to the reaction

$$C + 2H_2 = CH_4.$$

According to this the value of $\frac{p\text{-}(CH_4)}{p\text{-}(H_2)^2}$ should be constant at any given temperature.

In all experiments, at pressures varying from 10 to 200 atms., a value which was constant within the limits of experimental error was always obtained for this ratio at any particular temperature, and when the same modification of carbon was used. In some experiments, where an amount of methane in excess of this value was added to the gas beforehand, decomposition took place until the same final value was obtained. Consequently this represents the true equilibrium constant.

The amount of methane which at atmospheric pressure is in equilibrium with hydrogen and graphite is at 1200° equal to 0.24 per cent., and at 1500° 0.07 per cent. For amorphous carbon, the "metastable" equilibrium values are 0.36 per cent. at 1200° and 0.18 per cent. at 1500°. At a pressure of n atmospheres, the ratio of methane is n times as great as at 1 atmosphere.

The values found in this work for the equilibrium constants in the case of carbon and graphite enable an approximate calculation to be made of the heat of reaction in the transformation of amorphous carbon into graphite. According to Berthelot,[1] at ordinary temperatures, this has the value 2840 cals. per gram atom. This value at first falls with increase of temperature and at some temperature below 1000° becomes zero. Consequently amorphous carbon is the stable form at this temperature, but not at ordinary temperatures. When heated above this stable point, it again becomes unstable, and consequently passes more or less rapidly into graphite with evolution of heat.

The heat evolved in this transformation at different temperatures can be calculated by means of a formula deduced by van't Hoff. In this $Q_{(t)} = RT\ln\frac{K_{(1)}}{K_{(2)}}$, where $Q_{(t)}$ is the heat of reaction at the absolute temperature T; R, the gas constant in calories (1.98); $K_{(1)}$ the equilibrium constant in the methane formula with amorphous carbon; and $K_{(2)}$ that with graphite. We have from the above results the following values for the heat of reaction at different temperatures:

TABLE IV.—PARTLY GRAPHITIZED CARBON.

Temperature				
Centigrade.	Absolute.	$K_{(1)}$.	$K_{(2)}$.	$Q_{(t)} = RT\ln\frac{K_{(1)}}{K_{(2)}}$.
1200°	1473°	0.004	0.00245	1480
1300°	1573°	0.003	0.0016	1950
1400°	1673°	0.0023	0.0011	2450
1550°	1823°	0.0019	0.0007	32.0

It has been shown by Kirchhoff that the heat of a chemical reaction changes with the temperature in the following manner:

$$Q_{(t)} = Q_{(o)} + T[c_{(f)} - c_{(p)}]$$

where c_f is the mean specific heat of the factors (in this case carbon), and c_p that of the products of the reaction (in this case graphite).

Since Q increases with the temperature, it follows that the mean specific heat of carbon at temperatures above 1100° is higher than that of graphite, and the difference increases rapidly with the temperature.

The values given by Kunz[1] for carbon and by Weber[1] for graphite show the opposite relation at all temperatures above 200° C., and are consequently not applicable at these high temperatures.

It would indeed follow from the values of Kunz and of Weber that amorphous carbon would be stable at all temperatures.

It was also found that no saturated hydrocarbon other than methane is produced or is stable at any temperature or pressure employed in this work.

MANCHESTER, ENGLAND.

[1] *Compt. rend.*, **108**, 1144 (1889).

GLASS FORMULAS: A CRITICISM.[2]

By ALEXANDER SILVERMAN.

Of the many manufacturing industries in which secret processes are developed, there is perhaps hardly another which equals that of glass manufacture, and there is little doubt in the minds of those familiar with its methods that the formulas in actual use may be counted by thousands or even tens of thousands. Each manufacturer has made some change in a formula, either to follow the dictates of his fancy, or on the basis of sound scientific principles. Most of these changes belong to the former class, hence the thousands of recipes.

Occasionally there appears on the market a new book on glass manufacture. This may belong to one of three classes: *First*, Publications dwelling entirely on technical principles; *Second*, Those dwelling to some extent on technical and scientific principles and furnish ing formulas; and *Third*, Books containing formulas only. The writer proposes to confine his attention to classes two and three, as he has found quite a number of unreliable recommendations made in books and journals of these types. The criticism is in some cases based on fixed scientific principles, but in most cases is backed by experiments conducted on a large scale, *i. e.*, not in small crucibles in the laboratory but in regulation pots in the factory.

As examples of batches which have failed to yield the results claimed for them by their donors the following are cited:

Hohlbaum, "Zeitgemässe Herstellung, Bearbeitung und Verzierung des Feineren Hohlglases," 1910.

Page 127.	Rosaglas Nr. 7.
Sand	100 Kg.
Kohlensaurer Baryt	16 "
Soda 98%	43 "
Gold	12 g.

Absolutely no sign of color was obtained though directions were followed implicitly. The writer of this paper has, in fact, not been able to obtain a gold ruby unless reducing agents were added, and then

[1] *Ann. Physik*, [4] **14**, 327 (1904); *Ber. d. chem. Ges.*, **5**, 303 (1872).

[2] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

only with great difficulty when a lime batch was employed.

On page 127, Rosaglas Nr. 8 is given the following formula from its analysis:

Sand	100 Kg.
Kohlensaurer Baryt	16 "
Soda 98%	43 "
Gold	12 g.

A reducing agent should have been employed, and as the analysis did not show its nature, an organic or volatile inorganic body, or a combination of the two should have been recommended.

Rosaglas Nr. 9, same page, was prepared according to the formula:

Sand	100 Kg.
Pottasche	34 "
Kalkspat	17 "
Selenig Saures Natron	120 g.
Arsenic	200 "

and yielded only the faintest tinge of pink.

On page 146 the formula for Granatrot Nr. 107 yielded a glass so soft that it ran from the blowpipe like water. It yielded not a vestige of color though this formula was employed as given:

Sand	100 Kg.
Soda	50 "
Zinkoxyd	25 "
Selen	1/2 "
Schwefel Kadmium	1 "

All glasses thus far given and those ruby glasses yet to be mentioned were "warmed in" repeatedly when no color made itself manifest on the first gathering and blowing. Pots were clayed up as tightly as possible and all precautions necessary for the proper working of ruby glasses were observed.

These batches serve as examples from the Hohlbaum publication.

The claim may be made that furnace conditions were not proper as evinced by the soft nature of Granatrot Nr. 107. The writer wishes to say that he also tried some of Professor Hohlbaum's Alabaster batches and found that they were sandy and would not melt completely though treated in the same furnace.

If the furnace was too hot for one and too cold for the other, it shows the importance of giving not only batches but furnace conditions necessary for the successful preparation of the glass.

This criticism and those yet to follow concerning publications by other authors are not to be construed as a reflection on the works referred to, many of which are most admirable in other respects, but are intended to point out their weakness in publishing a lot of formulas, many of which will not work out in practice according to the directions accompanying them. The argument may also be made that many formulas are valuable trade secrets and dare not be published. That is no excuse for publishing poor ones, or even good ones with some important direction withheld.

Schnurpfeil, in "Die Schmelzung der Hohl, Schliff, Press, Tafel und Flaschenglaser," gives the following formulas which when tried yielded colorless glasses:

Page 97.	Rosarot 80.	Rosarot 81.
Sand	100 Kg.	100 Kg.
Soda	35 "	15 "
Kalk	14 "	18 "
Selen	55 g.	15 "
		100 g.

Rosè oder Rosenrot. 82.		Rosa. 83.
Lead	100 Kg.	100 Kg.
Pottasche	15 "	32 "
Soda	15 "	15 "
Marmor	12 "	30 g.
Saltpeter	1/4 "	
Selen	125 g.	

In none of the preceding four batches is a reducing agent employed, though this is essential for the production of a red color by selenium and in 82 the author even recommends the use of the oxidizing agent "saltpeter."

In *Sprechsaal*, 1911, page 706, in the second answer to question 183, a batch is recommended in which litharge is used for a selenium-red glass, in presence of a reducing agent. With lead and a reducing agent present selenium has a tendency to blacken glass just as does sulphur or its compounds. The writer has noticed some five or six batches recommended in various publications, in which lead compounds are used with selenium, but objects to all of these because of the danger of formation of lead selenide. In the third answer to question 183, same publication, a gold ruby batch is recommended without a reducing agent and in the fourth answer a lime-selenium batch is given. According to trials made, neither of these will work. The writer's statements regarding selenium glasses are largely corroborated by Dipl. Ing. Fritz Kraze in his article entitled "Selenglas" which appeared during the current year in numbers 14 and 15 of *Sprechsaal*.

Examples thus far given are confined to red or ruby glasses of the gold and selenium types. On numerous occasions copper-ruby batches have been published in which no reducing agent was prescribed. Many of the copper-ruby batches contain reducing agents in insufficient quantity, thus yielding green glass in which no amount of reheating will produce a red color.

Ruby formulas have been made an example of, because the most glaring and most numerous mistakes occur in that class. Next in order are the opal and alabaster glasses, and no class escapes entirely, not even the colorless transparent glasses.

To continue to cite incorrect formulas would only make this article monotonous. Even Henrivaux in his admirable volume has given formulas which do not yield the practical results claimed for them, and if all batches given in every other glass publication now in the market were tried not many would be found invulnerable. Several books containing only batches have been published anonymously, and one or two by men who claim to be expert glass-makers. Few of these batch books contain much that is worth trying. Some formulas are wrong in principle, others in the proportion which the raw materials bear to each other. If subjected to a close scrutiny hardly a single publication containing fromulas would go unscathed.

The writer's object in disclosures here made is to bring

glass manufacture and glass literature to the high plane occupied by other exact sciences. If the worthy gentlemen whose publications have been criticized and others, whom the limits of this article have not included, will coöperate by publishing only formulas which are known to be reliable, and will give proper directions for their use, they will materially assist in raising the plane of this important branch of science.

UNIVERSITY OF PITTSBURGH,
PITTSBURGH.

ON THE DENSITY OF SOME BORATE AND SILICATE GLASSES.

By Edwin Ward Tillotson, Jr.

Received July 1, 1912.

In a former paper[1] from this laboratory, attention was called to a method for calculating the approximate density of silicate glasses, and new density factors were proposed for several of the glass-forming oxides. In calculating the density of some borate glasses prepared in this laboratory, it became evident that the density of boric trioxide in the glass is somewhat greater than the figure (1.9) given by Winkelmann and Schott.[2] Comparison with other published data, giving weight to the more careful measurements of density, showed 2.24 as the most probable value for the density of boron trioxide in these glasses.

Table I shows the composition, the observed and calculated densities of several borate glasses from various sources. Table II shows the values for the density

TABLE I.

	Percentages.		Density.		
	B_2O_3.		Observed.	Calculated.[5]	Calculated.[6]
$Ca(BO_2)_2$	55.5	CaO 44.5	2.771[1]	2.50	2.807
$Mg(BO_2)_2$	63.6	MgO 36.4	2.520[1]	2.40	2.667
$Zn(BO_2)_2$	46.2	ZnO 53.8	3.320[1]	2.99	3.358
$Sr(BO_2)_2$	40.3	SrO 59.7	3.254[1]	....	3.258
W 11	41.0	ZnO 59.0	3.527[2]	3.17	3.532
W 16	42.8	Al_2O_3 5.2 PbO 52.0	3.691[2]	3.42	3.785
$BaO2B_2O_3$	46.37	PbO 53.63	3.522[3]	3.12	3.526
$BaO4B_2O_3$	63.40	PbO 36.60	2.922[3]	2.595	2.982
$Na_2B_4O_7$	69.3	Na_2O 30.7	2.370[4]	2.01	2.387

[1] *Tamman-Krystallisieren und Schmelzen*, p. 50.
[2] Winkelmann and Schott, *loc. cit.*
[3] Tillotson.
[4] Day and Allen, "Isomorphism and Thermal Properties of the Feldspars."
[5] Using Winkelmann's factors.
[6] Using modified factors.

TABLE II.

	Winkelmann factors.	Modified factors.
SiO_2	2.3	2.3
B_2O_3	1.9	2.24
Na_2O	2.6	2.8
CaO	3.3	4.1
MgO	3.8	4.0
Al_2O_3	4.1	2.75

employed by Winkelmann and Schott and those now proposed for giving a more accurate calculated value of the density of the glass.

Inspection of the figures in Table I shows that in the case of the carefully prepared borates the observed and calculated densities are in good agreement. Tamman[3] observed that in the preparation of these borates by fusing boric acid with the corresponding carbonates, it was difficult to drive off the last traces of carbon dioxide. This phenomenon was not observed in the preparation of the barium borates in this laboratory, although it was difficult to obtain borates containing high percentages of B_2O_3, free from minute bubbles, on account of the high viscosity of the melt. This doubtless explains some of the lower values for the observed density.

The density of sodium oxides in silicate glasses is apparently somewhat greater than that assigned to it by Winkelmann. In the following glasses the density was calculated, using 2.8 for sodium oxide:

	Percentages.						Density.	
No.	SiO_2.						Obs.	Calc.
W 25	71.0	ZnO	12	Na_2O	17.0		2.572	2.566
W 8	68.3	ZnO	5.0	Na_2O	10.8		2.629	2.639
		Al_2O_3	1.0	PbO	8.1			

This is further illustrated by the soda barium silicates shown in Table III.

TABLE III.

SiO_2. Per cent.	BaO. Per cent.	Na_2O. Per cent.	Density. Found.	Density. Calc.[1]	Density. Calc.[2]	Error.[1] Per cent.	Error.[2] Per cent.
74.50	...	25.50	2.437	2.37	2.41	+2.0	+1.0
66.15	13.00	20.85	2.64	2.59	2.625	+2.0	+0.6
61.70	19.10	18.50	2.752	2.725	2.755	+2.0	—0.2
53.00	33.60	13.40	3.06	3.03	3.055	+1.0	+0.1
71.70	5.65	22.65	2.491	2.45	2.50	+1.4	—0.2
67.60	12.55	19.85	2.633	2.57	2.615	+2.4	+0.7
64.55	18.45	17.00	2.759	2.69	2.72	+2.5	+1.4
61.30	24.20	19.50	2.824	2.80	2.83	+0.8	—0.2
58.30	29.70	12.00	2.934	2.925	2.96	+0.3	—0.9
55.34	35.10	9.56	3.072	3.05	3.08	+0.7	—0.2
52.46	40.60	6.94	3.212	3.195	3.22	+0.5	—0.2
49.95	46.00	4.55	3.367	3.35	3.37	+0.5	—0.1
46.91	50.80	2.29	3.476	3.50	3.51	—0.8	—1.1
44.25	55.75	...	3.65	3.67	3.69	—0.5	—0.5
79.00	5.15	15.85	2.46	2.43	2.455	+1.2	+0.2
75.85	9.35	14.80	2.514	2.50	2.523	+0.6	—0.4
67.45	20.35	12.20	2.722	2.72	2.73	+0.1	—0.3
62.60	26.60	10.80	2.845	2.84	2.87	+0.2	—0.9
57.20	33.60	9.20	3.06	3.01	3.04	+1.6	+0.7
51.14	41.50	7.36	3.224	3.265	3.245	—1.3	—0.9
36.84	60.40	2.76	3.95	3.88	3.90	+1.8	+1.2

[1] Using Winkelmann's factors.
[2] Using modified factors.

It will be seen that the observed and calculated values for the density of these silicates are in very good agreement and as the compositions of the glasses vary over wide limits, it is evident that the method is capable of giving excellent results with a large variety of glasses.

SUMMARY.

1. The densities of some pure borate glasses have been examined and an empirical factor determined for the density of B_2O_3 in the glass. The factor adopted is 2.24 instead of 1.9 as given by Winkelmann.

2. The densities of some soda barium glasses have been studied and the factor 2.8 for the density of Na_2O has been adopted in place of 2.6 employed by Winkelmann.

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[1] THIS JOURNAL, **3**, 897 (1911).
[2] *Ann. d. Phys. und. Chem.*, **49**, 401 (1893); **51**, 697 (1894); "Jena Glass and Its Industrial Application," Hovestadt (English Edition), p. 148.
[3] *Krystallisieren und Schmelzen.*

EXTRACTION OF THORIA.[1]

By Charles Baskerville.

Thorium dioxide is obtained in the main from monazite sands, which in round numbers may be said to have this composition:

	Per cent.
P_2O_5 (phosphates)	29
Ce_2O_3 (earths)	31
Di_2O_3 (earths)	31
SiO_2 (silicates)	1.50
ThO_2 (silicates and perhaps phosphates)	6.5

In the winnowing it is necessary to get rid of the phosphorus compounds as they materially interfere with the efficiency of the thoria when used for mantles. This is usually accomplished by converting the earths into insoluble oxalates after solution of the sand. Other methods have been proposed and some are now used commercially for avoiding this by fusion with alkaline carbonates and leaching the phosphates out with water, dissolving the residue in suitable acids, and then making the separation of the earths.

Troost[2] prepared thorium carbide (ThC_2) by heating the oxide with carbon. Moissan and Etard[3] made elaborate studies on the formation and properties of thorium carbide. Muthmann, Hofer and Weiss[4] fused monazite sand with carbon and dissolved the carbides and phosphides obtained in hydrochloric acid. Whereas the objectionable phosphoric compounds are removed in this manner, other practical difficulties arise, one being the hardness of the product, which involves expense in grinding the fused production.

The work of Kress and Metzger[5] indicates that thorium does not occur as the silicate in monazite. It is a fact, however, that silica or silicate is a constant but variable constituent of the sand and must be taken care of whatever means of extraction is applied. When the carbides are made by electric fusion of the sand with carbon, some silicon carbide is produced which cuts the grinding machinery in the later process of pulverizing. We have found that the addition of a small amount of fluorspar reduces this difficulty, yet the expense of some grinding remains.

In order to reduce this expense to a minimum, I decided to deliberately produce calcium carbide within the mass, which, when thrown into water, would disintegrate.[6] Although Moissan has shown that thorium and the rare earth(?) carbides are attacked by water, the speed of the reaction is very much less than with calcium carbide and is also much dependent upon the fineness of the particles. Hence comparatively little of the thorium and rare earth(?) carbides would be decomposed by such treatment. Many experiments were carried out, with theoretical and practical mixtures, in various types of furnaces (Stockem, Moissan, Héroult, and resistance), with direct and alternating currents. The numerous experimental details[7] need not be recited. Suffice it to say that a satisfactory charge may be with a sand of the approximate composition given above as follows:

	Lb.
Monazite sand	1.0
Carbon (petroleum coke)	1.10
Lime	0.80
Fluorspar	0.15

The best results were obtained with such charges by using a current of 35 volts and 125 amperes for one and one-half hours.

The procedure is as follows:

The mixture (unground sand being used) is made according to the principles outlined above and then subjected to electric-heat until phosphorus ceases to come off.[8] The mass is allowed to cool and then to decompose slowly by exposure to the air or quickly by placing in water. In the latter case the acetylene may be utilized, the mass falling to a fine powder. The dissolved and suspended calcium hydroxide are removed by washing. The residue is treated with hydrochloric acid and the thorium separated from the solution by sodium thiosulphate or other methods. This process is controlled by the Welsbach Light Co., of Gloucester City, N. J., and is published with their consent and approval.

College of the City of New York.

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

[2] *Compt. rend.*, **116**, 1227 (1893).

[3] *Ann. chim. phys.*, [7], **9**, 302 (1896); [7] **12**, 427 (1897); *Compt. rend.*, **122**, 573, 1462 (1896).

[4] *Ann.*, **320**, 260 (1901); German Patent 129,416, Aug., 1901.

[5] *J. Am. Chem. Soc.*, **31**, 640 (1909).

[6] Application for letters patent on this method of disintegration of fused masses has been made.

THE PRODUCTION OF AVAILABLE POTASH FROM THE NATURAL SILICATES.[3]

By Allerton S. Cushman and George W. Coggeshall.

The great demand which has recently arisen for an American supply of potash in available form for agriculture, has stimulated not only the search for new sources of this material but also experiments on a large and practical scale of operation, in the attempt to develop a method of making the vast supply of potash locked up in feldspars and feldspathic rocks either directly water-soluble or sufficiently soluble in dilute acids to insure a product which shall be useful as a fertilizer. The natural silicates commercially available as sources of potash are chiefly orthoclase and leucite. Both of these minerals are potassium-aluminum silicates. The theoretical formula for orthoclase is written $K_2O.Al_2O_3.6SiO_2$, and for leucite $K_2O.Al_2O_3.4SiO_2$. The principal sodium feldspar, albite, has the theoretical formula $Na_2O.Al_2O_3.6SiO_2$. It is well known that these feldspars run into and substitute each other in various proportions so that the products from different quarries will vary widely in respect to their soda and potash contents. There is an enormous supply of feldspar in the United States, both east and west, which could be made economically possible as a source of potash supply, provided the cost of production can be made low enough to compete with the potash-holding manure salts which are at present so largely imported from Germany. Although it must be admitted that the im-

[1] The experimental work was done by Mr. S. G. Warner of my staff.

[2] This phosphorus may be condensed.

[3] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

ported salts are richer in potash than any product that can ever be made from American feldspars, it should also be remembered that the crude German manure salts contain large quantities of chloride, and sulphates of elements which are not only undesirable in the fertilizer but which may do actual harm under certain conditions. It is this fact which gives encouragement to the attempt to produce from American feldspars a straight potash fertilizer which could be used in exactly the same way that hardwood ashes have been found useful.

Six general methods have been proposed for decomposing the natural silicates, in the effort to obtain water-soluble potash salts.

I. ADAPTATION OF NATURAL AGENCIES.

In the processes of Nature, the slow action of moisture and atmospheric agencies, including the action of carbonic acid gas, is known to have a decomposing or kaolinizing action upon the feldspars. Immense deposits of feldspar and granitic rocks have thus been decomposed, with the formation of large beds of kaolin and clays from which the potash has been leached into the surrounding valley. For this reason, the valleys between feldspathic and granitic hills are usually highly productive of the crops which require large amounts of potash, such as tobacco, potatoes, large fruits, berries, etc. There have been a few processes proposed, which depend principally upon the natural reactions hastened by pressure and other agencies. In 1904 Blackmore (U. S. Patent 772,206) proposed the action of carbon dioxide gas under five hundred pounds pressure upon a cream of the ground mineral, repeated intermittently for several hours, in the attempt to produce a yield of carbonate of potash. Ten years earlier the same experimenter (U. S. Patent 513,001) had proposed using lime, calcium chloride and steam pressure in an autoclave to produce chloride. In 1910 Coates (U. S. Patent 947,795) proposed the addition of bacteria for the decomposition of feldspar. In 1910 Carpenter (U. S. Patent 959,841) proposed to heat the mineral intensely and cool suddenly by plunging in water, in the effort to render the feldspar amorphous, in the hope of making it more available for plant growth. None of the above processes have as yet been shown to possess industrial possibilities.

II. WET PROCESSES OF A CHEMICAL NATURE.

Levi in 1904 (French Patent 344,246 and English Patent 13,875) and Piva in 1905 (French Patent 351,338) proposed methods for treating leucite by means of solutions of alkali or alkali earth hydrates, generally under increased pressure. The same general method for treating feldspar was claimed by Swayze in 1907 (U. S. Patent 862,676) and by Gibbs in 1909 (U. S. Patent 910,662).

Also Gibbs in 1904 (U. S. Patents 772,612 and 772,657) proposed a process of treatment with hydrofluosilicic acid, and subsequently with sulphuric acid, in order to produce potassium sulphate. In 1907 Cushman was granted U. S. Patent 851,922, a public patent which proposed the sludging of finely ground feldspar with water, the addition of a small amount in hydrofluoric acid and electrolyzing the mixture of wooden cells provided with wooden diaphragms. Under this process both potassium and aluminum hydrate passed through the cell diaphragm into the cathode compartment. This process, although perfectly practical, has not yet been made commercially possible owing to the high cost of hydrofluoric acid and the large amount of by-products formed in the process. None of the above processes have as yet been made commercial possibilities.

III. DRY PROCESSES OF A CHEMICAL NATURE, IN WHICH THE POTASH SALTS ARE VOLATILIZED.

In processes of this nature, fluxes, and in some cases fuel, for reducing purposes are ground and mixed with the feldspar, the mixture being subsequently heated until the potash salts are volatilized and collected either in the stack dust or partially collected from the gases by passing them through or over water. Swayze in 1905 (U. S. Patent 789,074) heated ground feldspar with gypsum and carbon, and proposed to collect the volatilized sulphate. Spencer and Eckel in 1909 (U. S. Patent 912,266) made a cement mixed with calcareous and siliceous fluxes and green sand, a natural potash-bearing iron silicate, clinkered the mixture in a rotary cement furnace, and obtained a Portland cement, at the same time collecting the potash in the stack dust and the flue gases. In 1911 Eckel (U. S. Patent 1,011,172) proposed a somewhat similar method but heated only high enough to drive off the potash salts and not high enough to clinker the mixture. Again, in 1911, Eckel (U. S. Patent 1,011,173) melted a mixture of green sand, limestone and fuel, tapped off the melted iron and slag, and recovered the potash salts from the flue gases.

Some of the processes under this heading have been tried on a large scale. No great difficulty is recorded in driving off the potash in the furnaces, but obstacles were encountered in the attempt to collect the potash from the gases. As a by-product operation in the manufacture of cements, these processes may yet come to be of some industrial importance.

IV. DRY PROCESSES WHICH PROPOSE TO SEPARATE POTASH AS HYDROXIDE OR CARBONATE.

The old method of Bickel, proposed in 1856 (U. S. Patent 16,111), which depended upon heating a mixture of feldspar, lime, and natural phosphate rock or guano to a bright red heat, has not as yet been proved practical or successful. The process of the Soc. Romana Solfati in 1905 (French Patent 352,275), which proposes the roasting of leucite with carbonate, hydrate or nitrate of soda and lime and subsequently the passage of steam through the roasted product to produce sodium aluminate and potassium carbonate, is possible from a chemical standpoint, but the high cost of operation has not permitted the process to come into commercial use.

V. DRY PROCESSES PRODUCING THE CHLORIDE.

These processes have been most experimented

with upon the mill scale of operation. In 1900 Rhodin (U. S. Patent 641,406 and *J. Soc. Chem. Ind.*, **20,** 439) proposed fritting feldspar with lime and salt. According to the published results, this experimenter obtained good yields although the process has not become a commercial success. In 1907 McKee (U. S. Patent 869,011) suggested heating a potash-bearing material containing mica with lime, salt and carbon in order to obtain a yield of potassium chloride. Cushman in 1911 (U. S. Patent 987,436) proposed mixing feldspar with lime and salts of a mineral acid capable of decomposing the silicate, giving the mixture special treatment previous to heating in a rotary furnace in order to produce the chloride. This method has been tried out on a large mill scale of operation, and the results obtained will be discussed later on in this paper.

VI. DRY PROCESSES PRODUCING SULPHATES.

In 1911 Thompson (U. S. Patent 995,105) proposed heating to a bright red heat a mixture of feldspar, sodium acid sulphate and sodium chloride, and subsequently leaching out the potassium sulphate produced. This experimenter claims that potassium chloride is first formed, which is subsequently changed to the sulphate by the action of the acid sulphate. It is stated that this process has recently been tried on a commercial scale of operation. Sodium acid sulphate is a by-product that is reasonably cheap although a large quantity is not available. The lack of an abundant supply of acid sulphite is perhaps the greatest drawback to the commercializing on a large scale of this process, although it is possible that it may still become of some industrial importance. Hart, in 1911 (U. S. Patent 997,761), proposed to fuse feldspar with some barium compound, such as the sulphate, together with carbon, to pulverize the cooled melt and subsequently to digest the product with sulphuric acid and thus produce in solution potash alum and a residue of barium sulphate and silica which is claimed to be useful as a paint pigment. Hart claims that some of the potash is volatilized during fusion. Since the fusion temperature is 1500° C., it is probable that a considerable portion of the potash does volatilize, and it is possible that this difficulty may interfere with the commercial success of the process. Wadman, in 1907 (U. S. Patent 847,856), proposed heating lepidolite with potassium sulphate and leaching the product with sulphuric acid in order to obtain sulphates of lithium and potash.

A chronological list of the patents which have been granted for the treatment of the silicates for the production of available potash is given in Table I.

It would appear that the most promising processes for making potash available from the natural silicates on a commercial scale of operation are those which are conducted in the dry way but without actual fusion of the reacting mixture. Potash salts volatilize readily at the high temperatures necessary for the fusion of the silicates, and the collection of the volatilized potash from the stack gases has not yet been carried out economically. A considerable portion of the potash does not settle in the dust chamber, and if water sprays are used for washing the gases, the potash solutions are very dilute and the cost of evaporation becomes prohibitive. Furthermore, water sprays are found to interfere with the draft regulation, even when the use of fans is resorted to. The maintenance of artificial draft is an expensive and difficult matter, and it is very likely to interfere with the proper control of the furnace temperatures. For work on the large scale of mill operation, a continuous process must be used, avoiding fusion and with the regulation of temperature to the exact point at which appreciable quantities of potash do not volatilize. The fluxes and reacting substances must be cheap, available in large quantity, and the yields of water-soluble potash salts must be high. The process which has seemed to us to give the most promise of successful adaptation to

TABLE I.—PROPOSED EXTRACTION PROCESSES CHRONOLOGICALLY ARRANGED.

PROCESS.		YEAR.	PATENTEE.	PRODUCT.
IV.	Lime, $Ca_3(PO_4)_2$, red heat	1856	Bickell	Potassium hydroxide
I.	Lime, powdered $CaCl_2$, H_2O, steam	1894	Blackmore	Potassium chloride
V.	Lime, salt, heat under melting	1900	Rhodin	Potassium chloride
II.	$Ca(OH)_2$ or NaOH, pressure 16 atmospheres	1904	Levi (leucite)	Potassium silicate
II.	H_2SiF_6 and H_2SO_4	1904	Gibbs	Potassium sulphate
I.	CO_2 500 lbs. pressure repeating	1904	Blackmore	Potassium carbonate
II.	(Leucite) KOH, NaOH, steam 25 atmospheres	1905	Piva	Potassium silicate Potassium aluminate
IV.	(Leucite) alkali, carbon, CaO red heat	1905	Soc. Romana Solfati	Potassium carbonate
III.	Gypsum and carbon, fuse, volatilize	1905	Swayze	Potassium sulphate
VI.	Lepidolite, K_2SO_4, H_2SO_4	1907	Wadman	Potassium sulphate
II.	Water and HFl electrolysis	1907	Cushman	Potassium hydroxide
II.	Heat alone then KOH solution	1907	Swayze	Potassium silicate Potassium aluminate
V.	"Containing mica" with CaO, NaCl and C	1907	McKee	Potassium chloride
II.	$Ca(OH)_2$ steam 150 lbs.	1909	Gibbs	Potassium hydroxide
III.	Green sand cement mix volatilize	1909	Spencer and Eckel	Potassium salts
I.	Bacteria action	1910	Coates	
I.	Intense heat, sudden cooling alone	1910	Carpenter	
V.	CaO, $CaCl_2$, etc., clumps, red heat	1911	Cushman	Potassium chloride
VI.	$NaHSO_4$, NaCl bright red	1911	Thompson	Potassium sulphate
VI.	Ba compound as $BaSO_4$ and C, fuse, H_2SO_4	1911	Hart	Potassium alum
III.	Cement mix but not over 900° C. with green sand volatilize	1911	Eckel	Potassium metallic Potassium sulphate
III.	Green sand, CaCO and C, melt, iron volatilizes	1911	Eckel	Potassium sulphate

commercial ends is that of Cushman (U. S. Patent 987,436) coupled with the method of preparation of the materials before furnacing, proposed and developed by Coggeshall (U. S. Patent 987,554).

This process has recently been given extensive trials on a large scale and interesting results have been obtained. The process consists essentially in powdering 100 parts of potash feldspar rock together with about 20 parts of lime and with or without 10 to 20 parts of rock salt. This powdered mixture is fed to the top of a moving drum about three feet in diameter, in a layer about half an inch deep. As soon as the layer is formed a strong solution of calcium chloride is applied from a series of small tubes. The calcium chloride at once unites with the lime, forming a so-called oxychloride cement and a large portion of the mixed powder is thereby at once formed into "clumps" or aggregates lying in a bed of surplus powder. As the drum revolves the bed is removed by a scraper to a belt that delivers the mixture to a screen which separates the clumps from the residual powder. The powder is returned by a screw conveyer and elevator to the hopper above the drum again. The clumps are about the size of peas and pass from the screen directly to a rotary kiln similar to those used in burning Portland cement. The kiln is heated by a blast of air and powdered coal in the usual manner.

The clumps pass regularly down through the increasingly heated portions of the rotating kiln and roll out at the end, practically without alteration in size and shape.

A large percentage of the total potash present in the feldspar is converted into potassium chloride during the heat treatment, and very little is volatilized. The dry clumps are of a pale yellow color outside, due to the iron in the ash of the bituminous coal used, but they are snow-white inside. The clumps are finally ground, producing a pale yellow material containing as much water-soluble K_2O as hardwood ashes, although the potash is in the form of chloride, and the product also contains considerable free lime. Up to the present time no attempt has been made on a large scale to leach out the soluble potash. The ground material is being given field tests as a straight potash fertilizer containing lime.

A RESUME OF THE LARGE SCALE EXPERIMENTS.

Potash feldspars were obtained from five different localities. Eleven carloads were used in the trials, amounting to a total of 385 tons. Each carload was ground and analyzed separately. The lowest in potash ran 6 per cent. K_2O and 3 per cent. Na_2O, the highest 11.3 per cent. K_2O and 3.1 per cent. Na_2O. The bulk of the spar ran 10 per cent. potash and 2 per cent. soda, and the results given in this paper were obtained on this 10 per cent. spar.

The lime was a high calcium quicklime, running about 90 per cent. CaO and 5.6 per cent. MgO.

The salt was rock salt from New York state and ran about 98 per cent. NaCl.

The calcium chloride was obtained from the Solvay Process Company. It was in the solid form and contained about 75 per cent. $CaCl_2$ and 25 per cent. water.

All of the above materials are available in very large quantities and at low cost. The calcium chloride is a by-product in the form of a moderately strong solution, and but a small portion is concentrated at the present time, as the chief use is for refrigerating purposes. Vast quantities are now run to waste. The solid form was used in these trials merely for convenience.

Many heats were made with mixtures of varying proportions, but the two mixtures used in the work here described were:

	Parts.		Parts.
Feldspar	100	Feldspar	100
Lime	20	Lime	20
Salt	10	Salt	20

The feldspar, lime and salt were separately crushed in gyratory crushers and rolls, and dried in a rotary drier. In continuous work the proper mixture would be made at this point by continuous weighing machines, but as a number of different mixtures were to be tried, each of the three raw materials was ground separately in Huntington mills and put into bins. This preliminary grinding of the feldspar and salt was to about 65 per cent. through a 100-mesh sieve, of the lime about 83 per cent. through the 100-mesh. The weight per cubic foot of each powder of the above fineness was then ascertained and measuring boxes were built so that the materials could be separately measured out and run together into a large mixing machine. Almost a ton was thus mixed each time. The mixture was then conveyed to a tube mill and further ground to a fineness of from 97 per cent. to 99.5 per cent. through a 100-mesh sieve, and then conveyed to the bin over the clumper and kiln.

The calcium chloride masses were broken up and thrown on a perforated grid in a large tank holding about 48 tons. Water was run in and the chloride dissolved most readily. The solution was run out when about 42 degrees Baumé into two large sump tanks, and brought to a constant strength of about 42 per cent. $CaCl_2$. This was then pumped up to an elevated tank and piped from there, through a constant-level tank, to the dropper tubes of the clumper placed in a row above the drum. This drum is 15.5 feet long and 3 feet in diameter, and is horizontal. There are 15 valved pipes, each one feeding an adjustable pipe holding 38 short dropping tubes of brass $^1/_{16}$ inch internal diameter, and set $^5/_{16}$ inch apart.

The finely ground mixed powder is taken from the bin by a chute, elevator and screw conveyor and distributed in a long hopper trough over the drum. It is taken from the trough by a roll device and spread evenly on the moving drum at its topmost point. The drum has a surface velocity of about 1.6 inches per second, the layer of powder advancing at this rate.

It was found that by dropping the liquid very rapidly upon the powder, the clumps could be made rapidly enough to give a full feed to the short rotary kiln when only one-third of the trough and droppers

and drum is used. A clumper drum 5 feet long produces every hour almost two tons of fresh clumps and considerably over a ton and a half of burned product with the kiln used in these trials. The excess of powder passes through a screen and goes to the same elevator which lifts the original material from the bin. The amount of actual $CaCl_2$ in the fresh lime is regulated to about 20 parts to each 100 parts of feldspar in the mixture. The clumps leave the screen in rounded form and flow directly into the kiln.

The reason for the above procedure will now be explained. In the first place, calcium chloride reacts very efficiently under these conditions with the feldspar by replacing the potassium with calcium, thus forming calcium silicate and potassium chloride. Anhydrous calcium chloride is expensive to produce and it is impracticable to grind it into a mixture on a large scale on account of the rapid absorption of moisture. Even if such a dry mixture could easily be made, its use would present certain disadvantages.

When a reaction between an ore and solid fluxes is produced by heating up to the fusing temperature, the reaction takes place on the surface of the particles alone and only at the points where the ore is in actual contact with the flux particles. Finer grinding will produce a larger surface area and thus a greater number of actual contact points, leading to a larger yield. There is, however, a degree of fineness beyond which it is not wise to go, on account of the cost of extremely fine grinding.

Another factor in the problem is brought out by the following experiments. A batch of ore and the theoretical amount of solid flux were ground together to just pass a 50-mesh sieve. This powder, when subjected to a certain heat treatment, gave a reaction yield of about 35 per cent. of the theoretical. The mixture was then ground to just pass a 100-mesh sieve and given the same heat treatment. A reaction yield was obtained of about 65 per cent. of the theoretical. The mixture was then ground to pass a 200-mesh sieve and again reheated as before. A smaller yield was obtained that when the material just passed the 100-mesh, although the particles were undoubtedly only half the average diameter with about four times the surface area and should therefore have had far more points of contact. Upon weighing equal volumes of the 50-mesh, 100-mesh and 200-mesh powders, it was found that the latter contained far less material and it became apparent that the 200-mesh powder consisted for over 54 per cent. of its volume simply of voids. Such finely ground powders are well known to "surge," that is, to show the tendency to flow like water through orifices in a manner resembling fountains. Material ground as fine as this is the cause of much trouble at spout slides and conveyors. Each particle of a material of this extreme fineness is undoubtedly surrounded by a film of air, the actual contact with the surfaces is lessened and friction almost eliminated. When allowed to flow into a bin, such a powder assumes an almost horizontal surface: there is practically no angle of repose. Unquestionably the lessened contact caused the low yields in the finely ground mixtures. Some of the finer material was briquetted and the subsequent heat yielded about 85 per cent. of the theoretical. Briquetting is, however, expensive and usually necessitates the addition of a binding agent foreign to the reaction.

As a result of these investigations, the method was developed for aggregating fine powders by dropping a suitable liquid upon an excess of the powder in such a way as to cause a temporary bond to form, thus practically eliminating the air films or voids around the individual particles and permitting actual surface contact. Under these conditions, with the same ore and flux used in the experiments described above, the same heat treatment yielded within 3 per cent. of the theoretical quantity present. This method of aggregating finely powdered materials previous to furnacing has already been used in several different ways. For example, in an ore mixture in which the flux material is an alkaline carbonate, such as sodium or potassium, which form crystalline salts containing water of crystallization, if the carbonate is used in the partially anhydrous condition and ground with the ore, water alone dropped upon the mix in the manner described formed at once a crystalline carbonate which binds the particles of ore and flux into separate clumps, which are hard enough to withstand screening, while the air films are practically eliminated. Using such a mixture and process as this, a practically theoretical yield was obtained, although the flux was used only in the exact molecular proportion called for by the reaction.

By this clumping process a very intimate contact of reaction of surfaces is readily obtained at a low cost. The quantity of flux necessary to complete the reaction is greatly reduced, the duration and temperature of the heat treatment is lessened and working with rotary kilns dusting and stack losses are almost entirely eliminated. The clumps are beautifully adapted to the feed mechanism of rotary kilns, as they flow easily, do not dust, and take the heat more evenly than fine powders. Now that the temperature conditions in rotary kilns can be accurately controlled, it would seem that many chemical and metallurgical reactions which are now performed by intermittent processes and with low yields could be much more economically carried out in continuous rotary kilns, taking advantage of this new method of forming aggregates previous to furnacing.

In the application of this method to the treatment of feldspathic rock, advantage was taken of the fact that a solution of calcium chloride acts upon dehydrated lime to form the oxychloride which is a strong cementing compound. It was found that the formation of calcium oxychloride gave a sufficiently strong bond to enable the aggregates to withstand the operation of screening and the burden in the kiln.

The theoretical quantity of calcium chloride flux required depends upon the total quantity of K_2O and Na_2O present in the mix, as it is evident that

the soda must also be liberated in proportion to its content. The feldspar ore used ran 10 per cent. K_2O and 2 per cent. Na_2O, which required theoretically 15.5 parts of calcic chloride. In all our trials some slight excess of calcium chloride has been used. The strength of the solution and the method of treatment has been such that about 20 parts of actual calcium chloride are present in the fresh clumps to every 100 parts of feldspar. The 20 parts of lime used is for the purpose of forming the aggregates, and this lime remains practically unchanged in the finished product. The presence of lime in a potash fertilizer will be found advantageous to most soils, and it is generally admitted that lime increases the manurial value of a fertilizer. If the object were to leach out the soluble potash salts from the product, a much smaller amount of lime could be used without interfering with the formation of hard clumps. The salt is added because it has been found to aid the heat reaction, probably mechanically as will be explained later on. The fresh clumps contain from 16 to 20 per cent. of moisture, which is, of course, evaporated in the upper part of the kiln.

The rotary kiln used in these trials was one of the old bottle-shaped cement kilns with a total length of slightly over fifty-five feet, the upper twenty feet having a diameter of 4 feet clear inside the firebrick lining, the lower portion widening out to nearly 6 feet inside diameter. The pitch was $^7/_8$ inch per foot and the most suitable speed was found to be one revolution in about $2^1/_2$ minutes.

The conditions of the heat treatment are very important. The kiln used was too short to yield the best results, and after the preliminary experiments changes were made which caused the material to take about $1^1/_2$ hours to pass through the length of the kiln. The temperature of the gases issuing from the upper end of the kiln were read continually with a thermocouple pyrometer fitted with a 15-foot fire end and temperatures were also taken from time to time at the firing platform. A furnace wall temperature of about 1370° C. is required for efficient burning of powdered bituminous coal. This is, however, much too high a temperature for potash work in a rotary kiln. This difficulty called for careful experimental investigations and adjustments of the heat treatment before the proper yields could be obtained. If a longer kiln had been available, there is every reason to believe that a more efficient use of the heat could have been obtained. The coal used was a fairly high volatile bituminous coal. It was ground to about 94 per cent. through a 100-mesh sieve and blown into the furnace under an air pressure of about ten pounds per square inch.

During the progress of the clumps down the kiln the following reactions probably take place: At the entrance to the kiln the water begins to evaporate. As the hotter zone is approached, the temperature rises high enough to melt calcium chloride and salt. Whether the calcium chloride is free to melt is not known to us, as the exact composition of the oxychloride compound formed has not yet been determined. The results of our work seem to prove that the reacting chlorine is more readily evolved from the oxychloride compound than it is from calcium chloride alone. The melting of the salt, however, continues the bond of the reacting particles, causing them to thoroughly "wet" each other, and from this point on the attack on the silicate proceeds rapidly. During the heating usually from 1 to 2 per cent. of Na_2O is volatilized.

When operating with no salt present, the yield of soluble potassium chloride was 47.5 per cent. of that originally present in the feldspar. On adding to the mixture 10 parts of salt to each 100 parts of spar, a test heat yielded 64 per cent., but of this 9 per cent. was lost by volatilization, giving a yield of 55 per cent. net in the final product. On adding 20 parts of salt to the mixture the yield grows to 69.2 per cent. with no volatilization and to 75 per cent. under heat conditions which caused a volatilization of 7 per cent., leaving a net yield of 68 per cent. of that originally present. In the case of clumps made from a mixture of 100 parts of feldspar containing 10 per cent. K_2O and 2 per cent. Na_2O, 20 parts of lime, 20 parts of salt and 20 parts of calcium chloride, the theoretical composition if no volatilization loss takes place is shown compared with the actual results obtained in the following table:

	Theory. Per cent.	Analysis. Per cent.	
Total K_2O.....	6.25	5.8	
Water-soluble K_2O....	....	4.2	Equals 6.65 per cent. KCl
Loss of K_2O.....	....	0.5	As KCl already formed
Total Na_2O.....	7.62	7.1	0.52 per cent. made into NaCl
Water-soluble Na_2O...	6.37	5.1	Showing 1.79 per cent. vaporized as NaCl or 26 per cent. of that present

This particular product contained 11.3 per cent. of free lime and total lime by analysis 15.5 per cent. There was also in this sample about 5 per cent. of free unchanged calcic chloride. The amount of calcic chloride in the various runs made up to the present time have been reduced gradually to about 1 per cent., and it is felt that in the future better conditions of heat treatment will make complete use of the calcic chloride and at the same time raise the yields of soluble potash. In later runs in which only 10 parts of salt were present in the mix, the theoretical and actual analysis of the product was as follows:

	Theory. Per cent.	Analysis. Per cent.	
Total K_2O.....	6.66	5.62	
Water-soluble K_2O....	....	4.5	Equals 7.12 per cent. KCl
Vaporization loss of soluble K_2O.....	....	1.04	As KCl already formed
K_2O insoluble in water.	....	1.12	
Total Na_2O.....	4.15		
Water-soluble Na_2O...	....	3.7	Showing 0.45 per cent. vaporized as NaCl or 11 per cent. of that present

This product contained 12.25 per cent. of free lime, the total potash rendered soluble was 5.54 per cent. of the product or 83.2 per cent. of the total quantity present, but as 15.6 per cent. had been volatilized the net yield in the product amounted to 67.6 per cent.

The material which was later made continuously according to the process described above carries 4.5 per cent. of water-soluble K_2O in the form of 7.12 per cent. potassium chloride and in addition to this the material carries only 1.12 per cent. K_2O insoluble in water. It is well known that a 2 per cent. citric acid solution will extract, when used according to the Wagner method, somewhat more K_2O than can be made directly water-soluble. This fact is of considerable interest when the product is to be used directly as a potash fertilizer.

CONCLUSION.

It is believed that under better conditions of heat treatment which can be obtained with longer kilns and with a somewhat different arrangement of the combustion chamber, slightly better yields than those reported can be obtained. It should be remembered that the kiln used in these experimental trials was originally designed for burning cement, but this type of kiln has long been superseded by improved forms. In order to get the proper heat treatment in the middle of the kiln to complete the reaction, it was necessary to have the upper part too hot. This condition will not maintain in a properly designed kiln. It is also believed that the use of oil as fuel would have allowed an easier regulation of the heat treatment but the trials so far undertaken have been made under conditions which were found available at the time.

The subject of the costs of this process and of the product cannot be gone into in detail at this time but a few general statements may be made. The production of water-soluble potash in feldspathic rock is essentially a low-grade proposition, and the commercial success of such a process depends upon the low cost of the various operations. The manufacture of a straight potash fertilizer containing as valuable ingredients only potash and lime, must be carried out on a very large scale and by the most modern methods of continuous operation. With regard to the clumping process, the trials have shown that this operation can be practically carried out as a continuous process and at an exceedingly low charge per ton of product.

The process may be directly compared with that of the manufacture of Portland cement. It is a little easier to grind feldspar and lime than the shales and limestones used in cement manufacture. Drying will cost no more. Chemical control of the raw mixes will not be more expensive and perhaps much less. Clumping, as has been shown, adds a very small charge to the expense of treatment. The cost of furnacing the feldspar mix will be less than similar charges in the cement industry, as the temperatures required are much lower and less coal is consumed. The product from the potash kiln is comparatively soft and pulverizes easily in hammer mills, while the charges on the cement industry for grinding clinker is an important item. Again, the softer potash product merely requires to be ground fine enough for use as a fertilizer, whereas cement clinker must be ground very fine and costs rise rapidly with increasing fineness. Repair bills in the case of feldspar treatment should be much smaller than in cement manufacture. The charge for raw materials is somewhat larger than in the case of cement, but this is more than met by the smaller costs of operation.

The potash fertilizer as now produced should be the equal in fertilizing value of the ordinary grades of hardwood ashes. The product carries practically the same content of water-soluble potash and a considerable percentage of free lime. There is every reason to believe that if the process becomes an industry the yields of water-soluble potash can be considerably improved. The material yielded is not a fused product, it is friable as an ash and it has the physical texture to make it a valuable aid to soil structure. The success of the product must, of course, depend upon the results obtained under test conditions in its experimental use as a fertilizer. If results are obtained which are as good or better than those which usually attend the proper use of high-grade wood ashes, it is believed that there should be no reason why this product cannot be successfully produced and introduced, especially in those parts of the country where potash feldspars, fuel and shipping facilities are available.

The results obtained on a number of experimental trials on a mill scale of operation show that it is possible to economically manufacture a potash fertilizer containing free lime from feldspar and for a sufficiently low cost to make worthy of consideration an industry based upon the method described.

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POTASH, SILICA AND ALUMINA FROM FELDSPAR.[1]

By EDWARD HART.

In a study of the commercial utilization of feldspar which I undertook several years ago, it soon became evident that the potash alone would not pay the cost of extraction. This is the cause of the commercial failure of all the methods heretofore proposed. It is necessary, therefore, to separate and put into marketable form the other constituents—silica and alumina—if our method is to be successful.

With this purpose in view I have finally worked out the following process which gives good prospect of commercial success:

The feldspar chosen should contain not much less than 12 per cent. potash. Spar of this quality can be obtained in quantity, but one of the pitfalls inventors must avoid is the expectation of getting spar containing the theoretical 16.9 per cent. of potash. The spar mixed with the proper amount of potassium sulfate and carbon is fused. The carbon added is so regulated that the resulting slag contains a considerable proportion of sulfids. This has the double advantage of saving a part of the sulfur, disengaged as hydrogen sulfid on dissolving in acids, which aids also in the complete decomposition by breaking apart the particles as it is given off. Experiments show that if a colorless slag is obtained of even higher alkali content

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

it is much less easily decomposed by sulfuric acid.

The slag so obtained must be very finely pulverized and treated in closed vessels with dilute sulfuric acid leaving behind a very pure silica which needs only washing and ignition to yield a marketable product fitted for the potter's use or for the manufacture of sodium silicate.

The solution contains potash alum and any small amounts of other metals such as iron, manganese and soda as sulfates. Lime is inadmissible, as the sulfate forms crusts on evaporating.

The solution on cooling gives at once crystals of alum, which washing with a little water and centrifuging renders marketable. Any iron present remains as ferrous sulfate in the mother liquor. Alum, however, is marketable only in limited quantity and must be, for the most part, converted into its constituents, aluminum and potassium sulfate. This is easily done by adding to the solution in a closed vessel potassium sulfid in slight excess when aluminum hydroxid mixed with a little sulfur precipitates in a form easily washed. This is dissolved in hot sulfuric acid, run through a filter and allowed to solidify. The potassium sulfate is obtained by evaporation.

Each ton of feldspar (12 per cent. K_2O) should yield 444 lbs. K_2SO_4, 2040 lbs. commercial aluminum sulfate (18 per cent. Al_2O_3), and 1300 lbs. SiO_2.

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COMPOSITION OF THE SALINES OF THE UNITED STATES.[1]

1. Rock Salt, Artificial Brines and Mother-liquors from Artificial Brines.

By J. W. TURRENTINE, with analyses by A. R. MERZ AND R. F. GARDNER.

Received August 7, 1912.

This report on the composition of the salines of the United States will embrace the following chapters: I, "Rock Salt, Artificial Brines and Mother Liquors from Artificial Brines;" II, Natural (Subterranean) Brines and Mother Liquors from Natural Brines;" III, "Brines from the Ocean and Salt Lakes;" IV, "The Utilization of the Salines of the United States as a Source of Potassium Salts;" and V, "The Occurrence of Lithium, Rubidium and Caesium in the Salines of the United States."

The present investigation was undertaken as a part of the general problem investigated by the Bureau of Soils of the United States Department of Agriculture, namely, to determine what sources of potassium salts could be developed in the United States. The intimate association of sodium and potassium in nature; in the feldspars and other of the older rocks; in the brine of the ocean and of numerous saline lakes and in the beds of deposited salts underlying the Magdeburg-Halberstadt region of Germany, warranted the belief that the two might be associated likewise in the rock salt and other salines of this country.

But slight information bearing on the problem was at hand. While numerous analyses of salines are to be found in the chemical literature, in most instances seemingly no attempt has been made to determine the potassium present therein. Since in such analyses any error is thrown upon the sodium, the presence of potassium therein would not be revealed unless tested for.

The investigation has consisted in a study of representative specimens of rock salt from those places where the beds have been entered; of brines from salt wells; of brine from gas and oil wells; of brines from salt lakes and of salt crusts from salt playas and marshes, and of the mother liquors and other concentrates from the salt refineries of the states east of the Rocky Mountains and from the "salt gardens" of the Pacific Coast.

GEOLOGICAL CONSIDERATIONS.

Rock salt has been found in large masses in three regions in the United States: (1) underlying an area represented by central and western New York, northeastern Ohio and probably the entire lower peninsular of Michigan; (2) underlying the State of Kansas and extending thence into Oklahoma; (3) in Louisiana and Texas. In Virginia and in certain localities of the west it is found in smaller local deposits, where, in the latter region, it has been deposited as the evaporation product of saline lakes.

The salt beds penetrated in New York, Ohio and Michigan are probably continuous, as they occur in the Salina group of rocks of the Upper Silurian, and the enclosing strata of the beds in the various regions for the most part have been pretty thoroughly correlated. The Salina formation appears as an outcrop in New York along a line extending east and west, and lying a few miles south of Lake Ontario. Thence it extends southward and dips to the south, disappearing beneath the mountains of western Pennsylvania. The formation as far south as Ithaca and Watkins in the State of New York is known to carry rock salt, though it is barren of salt in Pennsylvania.[1] The Salina rocks extend westward into Ohio until the eastern slope of the Cincinnati axis is encountered. The rock salt strata disappear east of that region. To the northwest, the western shores of Lake Michigan mark the limits of the Salina. To the north and northeast their limits are undetermined. Salt is being obtained from this formation at Goderich, in Ontario Province, Canada.

Two theories have been advanced to account for the formation of the rock salt of the Salina strata. These theories are at variance in that one supposes a marine origin and the other, a continental origin. The former describes the Salina sea as an arm of the ocean, separated from the ocean by bar-reefs or flats over which great tidal waves flowed into the bay. As the period was one of great aridity, only salt water, in the manner mentioned, entered the sea. Concentration through evaporation continued to saturation with respect to sodium chloride, whereupon that substance was deposited. Later, apparently, before the concentration with respect to the other saline constituents of ocean water became great enough to cause their deposition, the period of aridity came to

[1] Published with the permission of the Secretary of Agriculture.

[1] Chamberlain and Salisbury, Geology II, p. 389.

an end and the succeeding strata were non-saline in character.

The continental theory of the formation of the Salina rocks supposes that the area which they now cover was an undrained basin. Into it flowed the waters from the surrounding drainage area with their burden of detrital matter. The latter was derived from the rocks of the preceding geological age, the Niagaran. These were calcareous and presumably carried about one per cent. sodium chloride. The insoluble matter was deposited to form the calcilutites of the lower Salina strata, while the sodium chloride remained in solution to form the brine of the mid-Salinan sea.

It is possible to form some idea of the relative merits of these theories from geo-chemical considerations. However, such a discussion would be foreign to the purpose of this paper, and for that reason must be omitted.[1]

In Kansas, rock salt is found lying between shales of the Permian formation, the Wellington shales above and the Marion shales and limestones below. Toward the eastern part of the state the beds of salt gradually grow thinner and eventually disappear within the borders of the state. To the north they probably in like manner disappear. The southern and western limits of the beds are undetermined.

But little is known concerning the geological history of the sea from which the rock salt of Kansas was crystallized.

The rock salt deposits of Louisiana have been described by G. L. Harris, in Bulletin **7,** of the Geological Survey of Louisiana. These deposits are peculiar in that they appear in huge, dome-like masses projecting toward the surface from great and unknown depths. Their upward thrust has lifted the surface, forming, in Southern Louisiana, so-called islands. These are of Quaternary origin, while the salt masses belong to the Tertiary period. They are supposed to rest on rocks of Cretaceous origin.[2]

Several theories have been proposed to account for the origin of the salt domes. Their formation is the result of, or has resulted in, enormous lifting forces. All things considered, it appears most probable that they have resulted from the exertion of enormous pressures upon rock salt masses in the lower strata, which have squeezed the more plastic rock-salt upward through the less plastic rocks. The rock salt deposits of Texas exhibit the same characteristics as do those of Louisiana.

The rock salt of the United States for the most part is gray in color. This color is attributable to occlusions of minute particles of argillaceous limestone and gypsum. Its intensity varies, accordingly, from the dense, opaque gray of the argillaceous limestone, impregnated with crystalline sodium chloride to the almost perfectly colorless and transparent masses of halite. Red halite is found in Michigan and Kansas. The blue color of halite has been explained as due to organic matter and to metallic sodium.[3]

[1] Cf. *Bull.* **94,** Bureau of Soils, U. S. Department of Agriculture.

[2] Lucas, *Trans. Am. Inst. Mining Eng.*, **29,** 462 (1899).

[3] Clarke, "Data of Geo-Chemistry," 2nd Ed. Cf. also references to literature, foot note p. 220.

TECHNOLOGY OF SALT.

A full discussion of the technology of salt manufacture could scarcely be considered a logical part of this paper. However, those operations affecting the composition of the brines are pertinent and, therefore, are given brief mention here. The statements made apply particularly to those salt manufactories of New York and Michigan which were visited in person by the author. From the nature of the case, however, the same statements must apply within limits likewise to the manufactories in the other states where salt is prepared from similar natural materials.

Rock salt is mined from the thicker beds by the simple and well known "chamber-and-pillar" method. The height of the working face is determined largely by the thickness of the stratum, or mass, of transparent salt.[1] From the mine the rock salt is hoisted to the upper of a series of crushers, in which it is reduced to the desired state of fineness. Some of the larger pieces of good grade salt are not crushed, but are used in the form in which they come from the mine for "salting" live stock. The finer grades are employed principally in refrigeration. The natural gray color of the rock salt is prejudicial to its acceptance as table salt.

Artificial Brines.—In most instances salt is removed from its beds in solution. This is accomplished by admitting water from the surface to the salt beds and allowing it to stand in contact therewith until saturation is reached. This brine is spoken of as artificial to differentiate between it and the naturally occurring subterranean brine. A hole is drilled to the beds, through which a pipe is sunk. This and the annular space between it and the casing of the boring constitute two courses, through one of which fresh water enters and through the other brine is withdrawn. Gradually a cavity in the salt stratum is developed. From the larger cavities brine of a high concentration may be pumped continuously and rapidly, since the brine pumped out in a given space of time is so small as compared with the total amount of solution in the cavity, that the issuing brine is practically a saturated solution.

The fresh water admitted to the cavity is, of course, of a lower specific gravity than the brine, and consequently lies on top of the brine. More rapid solution therefore must take place from the upper portion of the walls of the cavity and hence, of the salt stratum. The composition of the artificial brine, then, can not be regarded in every case as necessarily representative of that of the entire stratum of rock salt dissolved. Where the Poli, or compressed air, system of pumping is employed, the agitation of the brine in the cavity may be sufficiently great to induce a more uniform dissolution of the cavity walls.

Preliminary Treatment.—From the wells, the brines enter settling tanks, where solid matter—small particles of argillaceous limestone and gypsum—is allowed to settle out. Following this, the brines may be run directly into evaporators, or may be subjected to

[1] Cf. Lucas, *loc. cit.*

treatment for the removal of any or all of the pernicious impurities, such as solid matter, hydrogen sulphide, iron, calcium and magnesium.

Hydrogen sulphide is removed either by allowing the brine to stand exposed to the open air, or by passing it over weirs or cascades, or through long troughs. With the removal of hydrogen sulfide, iron, present originally as ferrous salts, is oxidized and may be precipitated by the hydrolysis of its salts or by the addition of milk of lime. Calcium and magnesium are removed partially by precipitation with applications of soda ash. A further and more perfect separation is obtained with sodium phosphate.

Evaporation is effected in one of three forms of apparatus or in combinations of the three: "English open pans," "grainers," and "vacuum pans." The "English open pan" is of sheet iron and is supported on brick pillars and arches directly over the fire box and flues of a furnace. "Grainers" are shallow pans of sheet iron or cement, heated by means of steam pipes. "Vacuum pans" are funnel-shaped vessels of insulated sheet iron, covered with a dome-like top and heated with steam coils. These are operated singly or in combinations of two or three, designated respectively as the "single-," "double-" or "triple-effect" system. The rate of evaporation is increased by reduced pressure.

The crystallized salt is removed from the open pans and grainers by rakes operated by hand or mechanically, and from the vacuum pans by bucket-conveyors with perforated bottoms. The mother liquor is removed from the salt on dripping boards, in drainage bins or in centrifuges.

Mother Liquors.—The treatment of mother-liquors varies from plant to plant and is determined as much by the purity of the original brine as by any other factor.

The precipitation of calcium sulfate on the bottom of the open pans and the coils of the grainers and vacuum pans acts as an effective heat insulator and interrupts the evaporation. To remove this coating it is necessary to empty the evaporator. In some plants at this stage the brine is allowed to run into drains and is lost. If the preliminary purification has been only slight, this stage of the operation may be reached quite early, and the amount of salt obtained may represent only a small proportion of that present in the brine. There is then but a slight concentration of the impurities in the solution. The other extreme is found in those plants where it is the practice to subject the brine to a careful preliminary purification. The mother liquor resulting may be so free from impurities that it is not discarded, but, instead, is allowed to mix with fresh volumes of brine.

It was found to be impracticable in most instances to secure accurate information concerning the ratio between the volumes of brine evaporated and the mother liquor resulting, or the degree of concentration. As the practice varied so widely from plant to plant, it was even less practicable to determine the average volumes from all the plants visited. In general, it may be said that where mother liquors are discarded, the degree of concentration in them is slight.

HISTORICAL.

A large number of analyses of the various salines of the United States are to be found scattered through the literature. Goessmann[1] has studied the composition of the salines of the Syracuse district of New York, while Engelhardt[2] has examined numerous brines from the Wyoming and Genessee Valleys and the Onondaga (Syracuse) district of New York. The rock salt of Kansas and the incrustations on the Kansas salt marshes have been analyzed by Bailey and Case.[3]

Harris[4] quotes from Eckel[5] analyses of rock salts from Ontario, New York, Virginia and Louisiana. Analyses of rock salts from various foreign sources have been tabulated by Fürer.[6] This author likewise quotes analyses of various brines. Goessmann[7] has reported the analyses of a bittern, or mother liquor, representing a high degree of concentration, from the Syracuse brines. Fürer[8] has tabulated analyses of German mother liquors.

THE COLLECTION OF SAMPLES.

The specimens of rock salt, artificial and natural (subterranean) brines and mother liquors from artificial and natural brines, whose analyses are reported in these papers, were collected for the most part during the summer of 1911.[9] The samples from New York and Michigan collected during the summer of 1911 were taken in person by Dr. W. C. Phalen, of the United States Geological Survey, and the author; those from Ohio, West Virginia, Kansas and Louisiana were collected by Dr. Phalen. Certain other samples of brines from various sources, such as the oil or gas wells, or borings for oil or gas, in addition to those from the refineries in operation at that time, were collected by correspondence by the Geological Survey. This collection was made, as was the collection during the summer of 1911, for the purposes of a systematic investigation of the salines of the United States occurring east of the Rocky Mountains.[10] The taking of the samples in this manner, it was found, could not be accomplished in accordance with standardized methods; hence the later collection of 1911.

In taking samples, requisite care was observed to secure portions that were representative, where that was considered desirable. Specimens of rock-salt were taken by cutting grooves from ceiling to floor. The procedure should have insured a sample which was representative, in a perpendicular direction, of the stratum worked. The resulting lot of salt was reduced by quartering to the desired bulk. Samples

[1] *Am. J. Sci.*, **42**, 211, 368 (1866); **44**, 77 (1867); **49**, 78 (1869).

[2] "Salt and Gypsum Industries of New York," *Bull.* **11**, New York State Museum, **3**, op. p. 38.

[3] Kansas Geol. Survey, *Bull.* **7**, 70, 73 (1902).

[4] "Rock-salt," La. Geol. Surv., *Bull.* **7**, 84 (1907).

[5] "Salt and Gypsum of Southwestern Virginia," U. S. Geol. Surv., *Bull.* **213**, 413, 415 (1902).

[6] Salzbergau Salinenkunde," **1900**, p. 29.

[7] *Loc. cit.*

[8] *Loc. cit.*, cf. p. 628.

[9] The year in which the samples were collected is indicated in the explanatory notes following each table of analyses.

[10] The samples from this collection are indicated in the explanatory notes accompanying the following tables thus: "1910."

of brine were secured in most instances at the outlet pipe of the wells; in other instances, from the settling tanks. Samples of bitterns, or mother liquors, were taken from the evaporators at points as far removed as possible from the point of entrance of fresh brine. Mother liquors representing the maximum concentration were sought. In instances samples were taken from the dripping salt.

ANALYTICAL METHODS.

The methods of analyses employed were those described in Bureau of Chemistry *Circular* **52** and recommended for the analysis of mineral waters. The methods were modified in certain particulars to eliminate certain laborious details of the operation. As lithium in no instance was present in amounts sufficient to introduce a serious error, its separation from sodium and potassium was not attempted.

ANALYTICAL RESULTS.

The results of the analyses of rock salts and of other solids are calculated to per cent. Those of brines and mother liquors are calculated to parts per thousand (liter). In uniting the acid and basic ions in accordance with the conventional methods of combination, lithium and potassium are united to chloride ions; the sulfate ions are joined to calcium, sodium and magnesium in the order named; the bromide ions are united to magnesium and to sodium; and the residual basic ions are united to chloride ions.

In the following tables, the failure to report an ion should be taken to mean that that ion was not determined. Failure to report the conventional salt should be understood to mean the absence of that salt.

TABLE I.—ANALYSES OF ROCK-SALTS FROM NEW YORK, MICHIGAN, KANSAS AND LOUISIANA.

B. of S. No.	1.	2.	3.	4.	5.	6.	7.	8.	9.
Serial No.	15.	16.	17.	24.	144.	146.	151.	152.	155.
K	trace	trace	trace	trace	trace	0.1	trace	trace	trace
Na	38.9	38.0	39.0	38.9	38.4	38.6	38.4	38.4	39.1
Ca	0.2	1.0	trace	trace	0.8	0.4	0.8	0.4	trace
Mg	1.0	0.1	0.2	0.3	trace	0.1	trace	0.3	0.1
Cl	59.6	59.7	59.3	59.8	60.0	60.1	60.00	60.2	59.9
SO_4	1.2	1.2	0.5	1.0	0.8	0.8	0.6	0.9	0.9

CONVENTIONAL COMBINATIONS.

KCl	trace	trace	trace	trace	trace	0.2	trace	trace	trace
NaCl	97.2	96.7	98.5	97.3	97.4	97.9	97.7	97.5	98.3
$CaCl_2$	0.6	1.2	trace	trace	1.5	0.3	1.2	0.3	trace
$MgCl_2$	0.4	0.4	0.8	1.2	trace	0.4	trace	1.2	0.5
Na_2SO_4	1.8	...	...	1.5	...	...	...	...	1.2
$CaSO_4$	trace	1.7	0.7	trace	1.1	1.2	1.1	1.0	trace

1. Retsof Mining Co., Retsof, N. Y. Rock salt from near floor at working face, Room 24. Bed being removed, 8 feet in thickness. 1911. R. F. Gardner, analyst.

2. Sterling Salt Co., Halite, near Cuylerville, N. Y. Rock salt dust from beneath main crushers. 1911. R. F. Gardner, analyst.

3. Sterling Salt Co., Halite, near Cuylerville, N. Y. Sample from working face, west side of Room No. 1, northwest. Sample taken from roof to floor through full depth of stratum worked. 1911. R. F. Gardner, analyst.

4. Detroit Mining Co., Detroit, Mich. Sample from roof to floor at working face. Representative of stratum being removed, 1911. R. F. Gardner, analyst.

5. Crystal Salt Co., Kanopolis, Kan. 1911. R. F. Gardner, analyst.

6. Royal Salt Co., Kanopolis, Kan. 1911. R. F. Gardner, analyst.

7. Bevis Rock Salt Co., Lyons, Kans. Sample from 16-foot bed. 1911. R. F. Gardner, analyst.

8. Bevis Rock Salt Co., Lyons, Kans. Fine salt screened from coarse. 1911. R. F. Gardner, analyst.

9. Avery Rock Salt Co., Avery Island, La. 1911. R. F. Gardner, analyst.

TABLE II.—ARTIFICIAL BRINES OF NEW YORK.

B. of S. No.	10.	11.	12.	13.	14.	15.	16.	17.	18.
Serial No.	3.	4.	9.	10.	17.	24.	28.	29.	43.
K	0.3	trace	0.8	0.5	1.8	12.0	2.0	0.4	0.2
Na	114.0	110.6	93.8	108.0	104.4	108.4	112.8	113.0	85.3
Ca	3.2	2.7	9.3	2.7	4.8	3.4	4.2	3.8	0.4
Mg	0.3	0.3	1.0	0.5	1.6	1.4	1.6	0.2	0.2
Cl	180.4	181.1	163.5	160.7	179.1	181.9	182.2	179.5	129.4
SO_4	2.3	2.4	0.9	3.1	1.6	2.4	3.4	2.6	3.8
Br	...	...	...	...	1.1	1.1	0.8	0.7	0.6

CONVENTIONAL COMBINATIONS.

KCl	0.6	trace	1.5	1.0	22.5	22.9	3.8	0.8	0.4
NaCl	289.3	287.8	238.0	284.2	265.0	725.2	286.4	286.5	212.0
$CaCl_2$	6.1	4.7	24.6	3.9	11.3	6.6	7.8	7.5	1.1
$MgCl_2$	1.2	1.2	3.9	2.0	0.8	trace	2.4	0.8	trace
Na_2SO_4	...	...	...	...	...	...	...	...	5.6
$CaSO_4$	3.3	3.4	1.3	4.4	2.3	3.4	4.8	3.7	trace
$MgBr_2$	...	...	...	...	2.5	2.5	1.8	...	...
NaBr	...	...	...	...	...	...	...	0.9	0.8

10. Worcester Salt Co., Silver Spring, N. Y. 1911. A. R. Merz, analyst.

11. Rock Glen Salt Co., Rock Glen, N. Y. 1911. A. R. Merz, analyst.

12. Star and Crescent Salt Co., Saltvale, N. Y. 1911. A. R. Merz, analyst.

13. Genessee Salt Co., Piffard, N. Y. 1911. A. R. Merz, analyst.

14. Watkins Salt Co., Watkins, N. Y. Sample obtained through Geological Survey. 1910. R. F. Gardner, analyst.

15. International Salt Co., Watkins, N. Y. Sample obtained through Geological Survey. 1910. R. F. Gardner, analyst.

16. Genessee Salt Co., Genessee, N. Y. Sample obtained through Geological Survey. 1910. R. F. Gardner, analyst.

17. Remington Salt Co., Ithaca, N. Y. Sample obtained through Geological Survey. 1910. R. F. Gardner, analyst.

18. Onondaga Pipe Line Co., Liverpool, N. Y. 1910. R. F. Gardner, analyst.

TABLE III.—ARTIFICIAL BRINES OF OHIO.

B. of S. No.	19.	20.	21.	22.	23.	24.
Serial No.	104.	106.	107.	109.	111.	116.
K	0.4	0.2	0.8	0.4	1.0	3.0
Na	123.0	117.2	126.8	122.1	128.2	122.0
Ca	1.0	0.8	0.4	0.6	trace	0.2
Mg	trace	trace	0.9	trace	trace	trace
Cl	189.4	176.8	195.8	184.6	189.5	189.4
SO_4	2.8	6.8	4.6	6.4	9.8	1.8
Br	trace	none	trace	none	0.7	trace

CONVENTIONAL COMBINATIONS.

KCl	0.8	0.4	1.5	0.8	1.9	5.7
NaCl	308.9	289.1	316.4	302.1	311.3	307.4
$CaCl_2$	2.8	2.2	1.1	1.7	trace	0.6
$MgCl_2$	trace	trace	3.5	trace	trace	trace
Na_2SO_4	4.1	10.1	6.8	9.5	14.5	2.7
$CaSO_4$	trace	trace	trace	trace	trace	trace
$MgBr_2$	trace	none	trace	none	trace	trace
NaBr	...	...	...	...	1.5	...

19. Colonial Salt Co., Akron, Ohio. Artificial brine from well No. 6. 1911. R. F. Gardner, analyst.

20. Columbia Chemical Co., Barberton, Ohio. Artificial ("hydraulic") brine. 1911. R. F. Gardner, analyst.

21. Columbia Chemical Co., Barberton, Ohio. Artificial ("cavity") brine. 1911. R. F. Gardner, analyst.

22. Cleveland Salt Co., Cleveland, Ohio. Composite artificial brine from 2 wells. 1911. R. F. Gardner.

23. Union Salt Co., Cleveland, Ohio. Artificial brine from one well. 1911. R. F. Gardner, analyst.

24. Ohio Salt Co., Wadsworth, Ohio. Composite, artificial brine from 2 wells. 1911. R. F. Gardner, analyst.

TABLE IV.—ARTIFICIAL BRINES OF MICHIGAN.

B. of S. No.	25.	26.	27.	28.	29.	30.	31.
Serial No.	21.	87.	50.	52.	54.	57.	60.
K	trace	trace	0.1	0.1	0.2	0.1	0.2
Na	114.5	119.2	113.7	113.4	112.3	114.4	113.4
Ca	0.6	1.4	1.8	2.1	1.9	1.8	1.2
Mg	1.0	0.4	0.4	0.4	0.7	0.8	0.6
Cl	179.0	185.0	176.9	176.9	175.9	178.6	178.0
SO_4	2.2	2.8	3.3	3.7	3.2	4.0	0.8
Br	trace	trace	...	...	...	...	trace

Conventional Combinations							
KCl	trace	trace	0.2	0.2	0.4	0.2	0.4
NaCl	290.6	302.6	288.6	287.8	285.0	290.4	288.1
$CaCl_2$	trace	0.6	1.1	1.7	1.7	0.3	2.2
$MgCl_2$	3.6	1.6	1.6	1.6	2.7	3.1	2.4
$CaSO_4$	3.1	4.0	4.7	5.2	4.5	5.7	1.1
$MgBr_2$	trace	trace	...	...	...	...	trace

25. Delray Salt Co., Delray, near Detroit, Mich. Artificial brines direct from well. 1911. R. F. Gardner, analyst.

26. Michigan Alkali Co., Detroit, Mich. Artificial brine from well. 1911. R. F. Gardner, analyst.

27. Louis Sands Salt and Lumber Co., Manistee, Mich. Artificial brine from wells. A. R. Merz, analyst.

28. R. G. Peters Salt and Lumber Co., East Lake, near Manistee, Mich. Composite artificial brine from six wells; contains hydrogen sulphide. 1911. A. R. Merz, analyst.

29. Filer and Son, Filer City, near Manistee, Mich. Artificial brine from wells. 1911. A. R. Merz, analyst.

30. State Lumber Co., plant No. 2, Manistee, Mich. Composite artificial brine from 2 wells. 1911. A. R. Merz and R. F. Gardner, analysts.

31. Stearns Salt and Lumber Co., Ludington, Mich. Composite artificial brine from 4 wells. 1911. R. F. Gardner, analyst.

Table V.—Artificial Brines of Michigan and Canada.

B. of S. No.	32.	33.	34.	35.	36.	37.
Serial No.	91.	93.	95.	97.	99.	101.
K	trace	1.4	2.4	trace	1.4	3.8
Na	120.6	78.2	123.3	121.3	110.1	119.6
Ca	0.8	17.8	0.8	0.6	6.4	1.4
Mg	trace	12.8	trace	trace	3.0	0.9
Cl	183.8	182.1	189.3	185.2	190.2	191.4
SO_4	4.4	4.2	4.0	3.4	3.6	2.8
Br	trace	1.7	0.9	none	none	1.0
Conventional Combinations.						
KCl	trace	2.7	4.6	trace	2.7	7.2
NaCl	300.9	198.5	306.4	303.8	279.4	303.5
$CaCl_2$	2.2	40.1	2.2	1.7	16.9	0.5
$MgCl_2$	trace	45.5	trace	trace	11.8	3.9
Na_2SO_4	6.5	...	5.9	5.0	...	...
$CaSO_4$	trace	7.5	trace	trace	0.9	4.0
$MgBr_2$	trace	3.9	...	none	none	1.8
NaBr	...	...	...	1.6	...	...

32. Diamond Crystal Salt Co., St. Clair, Mich. Brine from a single well. 1911. R. F. Gardner, analyst.

33. Davidson, Wonsey Co., Marine City, Mich. Brine from two wells. 1911. R. F. Gardner, analyst.

34. Michigan Salt Works, Marine City, Mich. Brine from Company's one well. 1911. R. F. Gardner, analyst.

35. Worcester Salt Co., Ecorse, near Detroit, Mich. Composite brine from two wells. 1911. R. F. Gardner, analyst.

36. Western Canada Flour Mills Co., Goderich, Canada. Artificial brine from Company's one well. 1911. R. F. Gardner, analyst.

37. Mulkey Salt Co., Detroit, Mich. Composite brine from three wells. 1911. R. F. Gardner, analyst.

Table VI.—Bitterns from New York Artificial Brines.

B. of S. No.	38.	39.	40.	41.	42.	43.	44.
Serial No.	1a.	2a.	4.	5a.	6a.	18.	32.
K	trace	trace	1.0	0.2	0.6	0.2	0.6
Na	117.0	109.6	109.1	114.9	111.4	73.2	112.0
Ca	4.8	4.0	10.3	5.4	8.2	5.3	0.8
Mg	2.2	0.8	1.6	0.8	0.6	0.7	0.8
Cl	187.9	172.9	191.1	185.4	185.6	122.8	173.4
SO_4	3.6	4.6	0.6	2.4	2.0	1.1	1.2
Br	1.1	0.9	...	0.8	2.0	...	0.6
Conventional Combinations.							
KCl	trace	trace	1.9	0.4	1.1	0.4	1.1
NaCl	296.8	277.1	276.9	290.0	280.8	185.8	284.4
$CaCl_2$	9.1	5.8	27.7	12.2	20.5	13.3	0.8
$MgCl_2$	3.1	3.1	6.3	3.1	2.4	2.7	trace
$CaSO_4$	5.1	7.1	0.9	3.4	2.8	1.6	1.7
NaBr	...	1.3	...	1.0	2.8	...	...
$MgBr_2$	2.5	...	...	...	...	...	...

38. International Salt Co., Myers, N. Y. Bittern after 22 hours' evaporation. 1911. R. F. Gardner, analyst.

39. International Salt Co., Myers, N. Y. Bittern. 1911. R. F. Gardner, analyst.

40. Remington Salt Co., Ithaca, N. Y. Bittern from evaporators on way to drums. Represents an evaporation of 50 tons original brine to 25 tons. 1911. A. R. Merz, analyst.

41. Remington Salt Co., Ithaca, N. Y. Bittern from centrifuges at 9 A.M., first hour of centrifuging. 1911. R. F. Gardner, analyst.

42. Remington Salt Co., Ithaca, N. Y. Bittern from centrifuges at end of centrifuging (7 hours). 1911. R. F. Gardner, analyst.

43. LeRoy Salt Co., LeRoy, N. Y. Bittern from (continuous) run-off. 1911. A. R. Merz, analyst.

44. Solvay Process Co., Syracuse, N. Y. Bittern from brine from 50-foot salt bed. 1910. R. F. Gardner, analyst.

Table VII.—Bittern from New York Artificial Brines.

B. of S. No.	45.	46.	47.	48.	49.	50.	51.
Serial No.	1.	2.	5.	6.	7.	11.	12.
K	1.7	2.8	1.9	9.4	1.8	1.3	2.2
Na	110.1	100.3	106.7	73.7	93.7	114.2	108.9
Ca	11.4	19.9	13.5	20.2	25.2	6.4	7.6
Mg	1.0	1.8	1.5	1.6	2.6	1.9	1.9
Cl	193.1	197.2	193.5	135.0	197.5	192.8	187.8
SO_4	0.7	0.5	0.8	2.2	0.4	1.2	1.3
Conventional Combinations.							
KCl	3.2	5.3	3.6	17.9	3.4	2.5	4.2
NaCl	279.2	255.1	270.8	144.7	230.0	289.7	276.3
$CaCl_2$	30.7	54.5	36.5	53.4	69.1	16.3	19.7
$MgCl_2$	3.9	7.1	5.9	6.3	10.2	7.5	7.4
$CaSO_4$	1.0	0.7	1.1	3.1	0.6	1.7	1.8

45. Worcester Salt Co., Silver Springs, N. Y. Bittern from vacuum pans. 1911. A. R. Merz, analyst.

46. Worcester Salt Co., Silver Springs, N. Y. 1911. Bittern from grainer No. 6. A. R. Merz, analyst.

47. Rock Glen Salt Co., Rock Glen, N. Y. Bittern, 10 days' evaporation in open pans. 1911. A. R. Merz, analyst.

48. Rock Glen Salt Co., Rock Glen, N. Y. Bittern, 6 weeks' evaporation in grainer, taken at time of run-off. 1910. R. F. Gardner, analyst.

49. Star and Crescent Salt Co., Warsaw, N. Y. Bittern from open pans, taken at time of run-off. Represents an evaporation of 85,000 gals. original brine to 350 gals. 1911. A. R. Merz, analyst.

50. Genesee Salt Co., Piffard, N. Y. Bittern from open pans, 36 hours' evaporation. Represents an evaporation of 30,000 gals. to 15,000 gals. 1911. A. R. Merz, analyst.

51. Genesee Salt Co., Piffard, N. Y. Bittern from grainer, 2 weeks' evaporation. 1911. A. R. Merz, analyst.

Table VIII.—Bitterns from Artificial Brines of Michigan, East Shore.

B. of S. No.	52.	53.	54.	55.	56.	57.	58.
Serial No.	22.	23.	26.	92.	94.	96.	102.
K	0.1	trace	0.4	trace	trace	2.0	1.6
Na	120.3	121.1	115.9	117.1	121.4	104.6	118.4
Ca	2.0	1.9	2.2	3.4	0.6	13.8	1.2
Mg	0.2	0.2	1.4	0.6	trace	2.7	trace
Cl	186.8	187.5	184.8	188.0	185.5	194.6	179.6
SO_4	3.8	3.4	3.6	2.0	1.8	0.6	4.6
Br	...	...	none	0.8	2.5	...	7.8
Conventional Combinations.							
KCl	0.2	trace	0.8	trace	trace	3.8	3.1
NaCl	305.3	306.9	295.0	296.5	304.2	265.9	289.9
$CaCl_2$	1.7	1.4	1.9	9.2	1.7	37.3	3.3
$MgCl_2$	0.8	0.8	5.5	2.4	trace	10.6	trace
Na_2SO_4	...	...	...	...	2.7	...	6.8
$CaSO_4$	5.4	4.8	5.1	2.8	trace	0.9	trace
NaBr	...	...	none	1.0	3.2	...	10.1
$MgBr_2$	...	...	none	...	...	...	...

52. Delray Salt Co., Delray (Detroit), Mich. Bittern, drippings from salt as conveyed from vacuum pans. Probably but slight concentration. 1911. A. R. Merz, analyst.

53. Delray Salt Co. Bittern from grainer, 12 days' evaporation. 1911. A. R. Merz, analyst.

54. Pennsylvania Salt Co., Wyandotte, Mich. Bittern from dripping vats. 1910. R. F. Gardner, analyst.

55. Diamond Crystal Salt Co., St. Clair, Mich. Bittern from grainer, 23 days' evaporation. 1911. R. F. Gardner, analyst.

56. Davidson, Wonsey Co., Marine City, Mich. Bittern, drippings from vacuum pan salt. 1911. R. F. Gardner, analyst.

57. Michigan Salt Works, Marine City, Mich. Bittern from grainer, 6 weeks' evaporation. 1911. A. R. Merz, analyst.

58. Mulkey Salt Co., Detroit, Mich. Bittern, 30 to 35 days' evaporation. 1911. R. F. Gardner, analyst.

TABLE IX.—BITTERNS FROM ARTIFICIAL BRINES OF MICHIGAN, WEST SHORE.

B. of S. No.	59.	60.	61.	62.	63.
Serial No.	27.	53.	56.	59.	61.
K	2.0	0.5	0.2	0.7	trace
Na	89.7	115.1	119.1	111.1	121.4
Ca	5.2	3.9	2.4	3.5	2.8
Mg	15.4	3.0	1.6	4.6	0.3
Cl	191.8	191.4	189.8	189.8	190.4
SO_4	3.2	2.3	3.4	2.3	2.4
Br	trace	...	...	...	..
CONVENTIONAL COMBINATIONS.					
KCl	3.8	1.0	0.4	1.3	trace
NaCl	227.9	292.0	302.1	282.8	307.4
$CaCl_2$	10 8	8.0	2.8	6.9	5.0
$MgCl_2$	60.4	11.8	6.3	18.0	1.2
$CaSO_4$	4.5	3.3	4.8	3.3	3.4
$MgBr_2$	trace	...	...	...	...

59. Filer and Son, Filer City, near Manistee, Mich. Drippings from salt. 1911. R. F. Gardner, analyst.

60. Peters Salt nd Lumber Co., East Lake, Manistee, Mich. Bittern from grainer, 19 days' evaporation. 1911. A. R. Merz, analyst.

61. Buckley, Douglas Lumber Co., Manistee, Mich. Bittern from grainer, 4 weeks' evaporation. 1911. A. R. Merz, analyst.

62. Louis Sands Lumber Co., Manistee, Mich. Bittern from grainer, 3 weeks' evaporation. 1911. A. R. Merz, analyst.

63. Stearns Salt and Lumber Co., Ludington, Mich. Bittern from grainer. 1911. A. R. Merz, analyst.

TABLE X.—BITTERNS FROM ARTIFICIAL BRINES OF CANADA AND OHIO.

B. of S. No.	64.	65.	66.	67.	68.
Serial No.	100.	103.	112.	117.	118.
K	1.4	2.8	1.2	0.7	1.8
Na	115.7	108.4	100.1	103.7	97.6
Ca	4.6	12.8	16.3	16.5	12.0
Mg	2.4	1.6	3.7	1.3	2.4
Cl	191.6	193.0	194.5	192.3	187.8
SO_4	3.2	5.0	0.7	1.1	1.8
Br	none	trace	trace	trace	trace
CONVENTIONAL COMBINATIONS.					
KCl	2.7	5.4	2.3	1.3	3.4
NaCl	293.7	275.2	254.6	263.4	263.0
$CaCl_2$	11.9	29.6	44.3	44.3	31.0
$MgCl_2$	6.1	6.3	14.5	5.1	9.4
$CaSO_4$	4.5	7.1	1.0	1.6	2.6
$MgBr_2$	none	trace	trace	trace	trace

64. Western Canada Flour Mills Co., Goderich, Canada. Bittern, 5 weeks' evaporation. 1911. R. F. Gardner, analyst.

65. Colonial Salt Co., Akron, Ohio. Bittern from grainer, $5\frac{1}{2}$ months' evaporation. 1911. R. F. Gardner, analyst.

66. Union Salt Co., Cleveland, Ohio. Bittern from grainer, 5 days' evaporation. 1911. A. R. Merz, analyst.

67. Ohio Salt Co., Wadsworth, Ohio. Bittern, 35 days' evaporation. 1911. A. R. Merz, analyst.

68. Ohio Salt Co., Wadsworth, Ohio. Bittern, from vacuum pan at boot. 1911. A. R. Merz, and R. F. Gardner, analysts.

TABLE XI.—BITTERNS FROM KANSAS ARTIFICIAL BRINES.

B. of S. No.	69.	70.	71.
Serial No.	140.	150.	154.
K	1.0	trace	0.2
Na	90.4	118.4	101.1
Ca	1.4	0.8	0.4
Mg	15.8	2.4	11.6
Cl	182.5	186.	182.0
SO_4	3.4	5.4	11.2
Br	0.9	trace	trace
CONVENTIONAL COMBINATIONS.			
KCl	2.0	trace	0.4
NaCl	229.3	293.4	242.9
$CaCl_2$	trace	2.2	1.1
$MgCl_2$	57.2	9.4	45.4
Na_2SO_4	...	8.0	16.6
$CaSO_4$	4.8	trace	trace
$MgBr_2$	2.1	trace	trace

69. Western Salt Works (Hutchinson Salt Co.), Hutchinson, Kans. Bittern from open pan, after 25 days' evaporation. 1911. R. F. Gardner, analyst.

70. Sterling Salt Co., Sterling, Kansas. Bittern from grainer after 30 days' evaporation. 1911. R. F. Gardner, analyst.

71. Orient Salt Co., Anthony, Kansas. Bittern from grainer after 8 days' evaporation. 1911. R. F. Gardner, analyst.

DISCUSSION OF RESULTS.

The analyses of the artificial brines show them to be remarkably pure solutions of sodium chloride, a fact to be expected from their origin. There are numerous minor differences between individual brines, and a small number of variations of greater importance. On the whole, one is surprised that the rock salt from the various deposits is of such a constant composition (assuming for the moment that the similarity between the artificial brines connotes an equal similarity between the various rock salts), until one remembers that a partial crystallization of sodium chloride from various sorts of solutions must, of necessity, give crystals of approximately similar composition. Whatever the nature of the sea, the sodium chloride crystallized therefrom should form crystal masses similar to those from a sea of widely varying composition. Only by a comparison of the occluded impurities can differences between the original brines, instrumental in the formation of the deposits, be detected. However, in the case of the brines examined in this investigation, the impurities occur in such small amounts and the difficulties of the analysis are such that a comparison of this nature appears scarcely warranted.

It is probable that the artificial brines are approximately saturated solutions of gypsum. In addition to the gypsum occluded by the rock salt, the solution in formation in the cavity in the salt strata in certain cases may be brought into contact with contiguous strata of gypsum. That the solutions from certain wells at times have been saturated with respect to gypsum is attested by the fact that the issuing pipes from the wells are lined by a sheet of crystallized gypsum.

The difference in conposition between rock salt and the artificial brines, prepared from rock salt, is only slight. That there is any difference at all is not a matter of surprise, when the conditions under which artificial brines are formed are recalled.

It will be noted that the ratio between the potassium in the original brine and the mother liquor resulting therefrom is not the same as that between the volumes of the original brine and resulting mother liquor. In other words, potassium has been eliminated from the solution at some stage or stages in the treatment. This is not explicable on the basis of crystallization, as the saturation point of any known potassium compound capable of existing in equilibrium with a solution of such a composition is not even remotely approached. The explanation, however, probably will be found in adsorption. The tendency exhibited by the potassium ion to be adsorbed by finely divided solids has been mentioned in previous paragraphs. It is believed that the potassium is eliminated little by little, adsorbed upon the surface of the crystalline sodium chloride.

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THE DETERMINATION OF PHOSPHORUS IN COMMERCIAL ACETYLENE.

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Received May 28, 1912

Acetylene that is prepared by the action of water upon calcium carbide almost always contains gaseous compounds of phosphorus that arise from the calcium phosphide in the carbide. If the acetylene is generated by dropping water upon the carbide, the high temperature resulting from the localized action of the two substances may give rise to a considerable amount of organic phosphorus compounds. On the other hand, if appreciable rise of temperature during the generation of the gas is avoided, practically all of the phosphorus in the acetylene is in the form of phosphine. The amount of phosphine in crude acetylene is quite variable, but it usually lies between 0.03 per cent. and 1.8 per cent.[1]

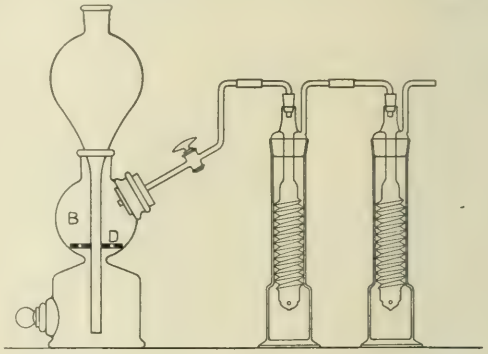
Of the methods that have been proposed for the determination of the gaseous compounds of phosphorus in acetylene, the combustion method developed by Eitner,[2] Keppeler,[3] and Fraenkel,[4] and the sodium hypochlorite absorption method of Lunge and Cedercreutz[5] are in most general use. The first of these methods, in which the phosphorus in crude acetylene is determined by burning the gas and ascertaining the phosphoric acid in the products of combustion, gives the total amount of phosphorus, whether it is present in the gas as phosphine or as organic phosphorus compounds. The acetylene is burned in an acetylene Bunsen burner under a cylindrical glass hood, and the products of combustion are drawn through an oxidizing solution, such as sodium hypochlorite or hypobromite. The resulting phosphoric acid is then determined by precipitation with "magnesia mixture." On account of the difficulty in regulating the pressure of the gas as it comes from the evolution apparatus, Fraenkel recommends that the acetylene from about 50 grams of calcium carbide be collected over a salt solution in a large tubulated bottle, and that the gas be then driven from this bottle through the burner. This necessitates the use of glass bottles of about 20 liters capacity, and if the acetylene is to be mixed with an equal volume of hydrogen before combustion, as Fraenkel recommends, the containers must be so large as to render them very unwieldy and quite expensive. Moreover, the accuracy of the determination of phosphorus in the gas will undoubtedly be affected by the reaction between the compounds of phosphorus and the confining liquid.

For these reasons the method of Lunge and Cedercreutz in which the crude acetylene is passed directly from the generating apparatus through a solution of sodium hypochlorite is to be preferred to the combustion method if it will yield accurate results. Objection has been raised to this absorption method because the acetylene is generated by dropping water on the calcium carbide, which gives rise to organic phosphorus compounds that escape complete oxidation. In seeking to improve this absorption method, the two points that present themselves are therefore:

(1) A method of generating acetylene that will avoid appreciable rise of temperature when the calcium carbide is decomposed, and

(2) An absorption apparatus that is more efficient than the ten-bulb tube used by Lunge and Cedercreutz.

The evolution of acetylene without marked rise of temperature was accomplished easily by the employment of a small Kipp apparatus about 40 cm. high, and with bulbs about 10 cm. in diameter. The annular space around the stem between the middle and bottom bulbs is covered with a perforated rubber disk, *D* (Fig. 1). A solution of sodium chloride, saturated at room temperature, is poured into the top bulb



until the end of the stem in the bottom bulb is covered with the liquid. A perforated stopper carrying a short glass tube is inserted in the neck of the top bulb, the stopper with exit tube and glass stopcock is inserted in the tubulus of the bulb *B*, and the further end of the outlet tube is connected with the absorption apparatus that contains the solution of sodium hypochlorite. Hydrogen gas is now passed into the upper bulb of the Kipp generator, and through the absorption apparatus to displace the air. About 50 grams of the calcium carbide under examination, broken into pieces about the size of a pea and sifted to remove the dust, is placed in a dry weighing tube which is at once tightly stoppered and weighed. When practically all of the air has been displaced from the Kipp apparatus by hydrogen, the stopper in the tubulus of the bulb *B* is removed, the contents of the sample tube is poured into the bulb and the stopper is at once reinserted. The current of hydrogen through the apparatus is continued for about five minutes, the stopcock then closed, and the stopper and tube are removed from the upper bulb of the Kipp generator. An additional amount of salt solution sufficient to cause the apparatus to function as a gas generator is then introduced into the upper bulb. The stopcock is now opened to such an extent that the evolved gases pass through the apparatus at a rate slightly faster than will permit of the bubbles being counted. Under these conditions the decomposition of a sample of 50 grams will be

[1] Vogel, *Handbuch für Acetylen*, page 234. The analyses given by Fraenkel, *J. Gasbel.*, **51**, 431 (1908), show from 0.024 to 0.057 per cent. by volume of phosphine in crude acetylene.

[2] *J. Gasbel.*, **44**, 548 (1901).

[3] *Ibid.*, **45**, 802 (1902).

[4] *Ibid.*, **51**, 431 (1908).

[5] *Z. angew. Chem.*, 651, **1897**.

effected in about two hours. The reaction between the salt solution and the calcium carbide proceeds at a uniform rate, and with no appreciable rise of temperature.

The absorption apparatus employed is a Friedrichs gas washing bottle modified so that the apparatus can easily be rinsed out with water at the close of the run. The absorbing solution is introduced into the outer cylinder to such height that it will stand at the top of the widened foot of the cylinder, and the spiral with the ground glass shoulder is then inserted. When a gas is passed into the bottle through the central tube, it follows the grooves of the spiral when it rises and pushes some of the solution ahead of it. These gas washing bottles are much more compact than the ten-bulb tube used by Lunge and Cedercreutz, and experiment has shown that the absorption attained by their use is surprisingly rapid and complete. The solution of sodium hypochlorite with which the absorption apparatus is charged is prepared by dissolving 15 grams of sodium hydroxide in 100 cc. of water, saturating the solution with chlorine, driving out the excess of chlorine with a current of air, and then determining the amount of sodium hypochlorite in the solution by treatment with hydrogen dioxide in a Lunge nitrometer. The solution is then diluted to three per cent. NaClO, and about 75 cc. of this solution is placed in each bottle.

After the decomposition of the calcium carbide is complete, the acetylene that remains in the generator is driven over into the absorption bottles by again passing hydrogen through the apparatus in the manner above described. The contents of the gas washing bottles are then transferred to a beaker, the bottles and inner tubes being thoroughly rinsed with distilled water: 10 cc. of concentrated hydrochloric acid is added to the liquid, which is then boiled until the odor of chlorine is no longer noticeable. Ammonium hydroxide is added to alkaline reaction and the phosphoric acid present is determined by precipitation with magnesia mixture, weighing as magnesium pyrophosphate.

The volume of phosphine to which the weight of magnesium pyrophosphate is equivalent may be calculated as follows:

$Mg_2P_2O_7 : 2\ PH_3 = 222.72 : 68.13$, or weight $Mg_2P_2O_7 \times 0.3059$ = weight phosphine.

Since one gram of phosphine occupies a volume of 657.9 cc. at 0° C. and 760 mm. pressure, volume of PH_3 in cc. = weight in grams $Mg_2P_2O_7 \times 0.3059 \times 657.9$ or, volume of PH_3 in cc. = weight in grams $Mg_2P_2O_7 \times 201.25$.

It is customary to report the results as the per cent. by volume of phosphine in the evolved acetylene. This necessitates the determination of the volume of gas that is liberated by the calcium carbide under examination. The most convenient method for making this determination is that proposed by Bamberger[1] who places a definite amount of the carbide in a weighed two-neck Wolff bottle of about 400 cc. capacity, and runs in upon the carbide an amount of a saturated solution of sodium chloride sufficient to entirely decompose the substance. The whole apparatus is weighed before and after the reaction, and the loss in weight equals the weight of the evolved gases, which are here assumed to consist entirely of acetylene. The total weight of the Bamberger apparatus before the decomposition of the carbide amounts to from 550 to 800 grams. This weight may be materially reduced by employing, in place of the Wolff bottle, an Erlenmeyer flask of about 250 cc. capacity. This is fitted with a two-hole rubber stopper into one opening of which is inserted the stem of a small separatory funnel of 125 cc. capacity; the other opening of the stopper carries a U-tube filled with calcium chloride. A sample of the calcium carbide amounting to about 50 grams is accurately weighed in a weighing bottle, and is then introduced into the flask. The stopper carrying the separatory funnel and the U-tube is then inserted, and the funnel is filled with a 20 per cent. solution of sodium chloride. The whole apparatus is then weighed on a balance accurate to 0.01 gram. The total weight of this modified form of the Bamberger device is approximately 300 grams. The salt solution is now allowed to drop slowly upon the calcium carbide, and, after decomposition is complete, dry air is passed through the apparatus to expel all of the acetylene. The apparatus is then again weighed, the difference between the two weighings giving the weight of the acetylene evolved. One kg. of chemically pure calcium carbide yields 405.93 grams of acetylene, equivalent to 348.4 liters of acetylene under standard conditions. Assuming that the loss of weight in the apparatus equals the weight of the acetylene evolved, the volume of the liberated gas may be calculated as follows:

$$\text{Weight of Sample} : \text{Weight } C_2H_2 = 100 : x$$

x = the weight of evolved acetylene expressed in per cent. of weight of the calcium carbide.

Since *pure* calcium carbide will yield acetylene amounting to 40.593 per cent. of the weight of the calcium carbide,

$$40.593 : \text{per cent. } C_2H_2 \text{ by weight} = 348.4 : x$$

x = the number of liters of acetylene evolved from one kilogram of the calcium carbide under examination, or the number of cubic centimeters evolved from one gram of the carbide.

From the above data the per cent. by volume of the phosphine in the acetylene may now be calculated. An example of such a calculation follows:

A. Determination of Phosphine.

Calcium carbide taken = 50.3548 grams.
Weight of $Mg_2P_2O_7$ = 0.0089 gram.

$$\text{cc. } PH_3 \text{ from 1 gram } CaC_2 = \frac{0.0089 \times 201.25}{50.3548} = 0.035 \text{ cc.}$$

B. Determination of Yield of Acetylene.

Calcium carbide taken = 41.071 grams.
Loss of weight of apparatus = 14.4885 grams.
41.071 : 14.4885 = 100 : per cent. C_2H_2 by wt.
Per cent. C_2H_2 by weight = 35.28.
40.593 : 35.28 = 348.4 : cc. C_2H_2 from 1 gram CaC_2.
Volume C_2H_2 from 1 gram CaC_2 = 300 cc.

$$\text{Per cent. } PH_3 \text{ by volume} = \frac{\text{cc. } PH_3 \text{ from 1 gram } CaC_2 \times 100}{\text{cc. } C_2H_2 \text{ from 1 gram } CaC_2} = 0.0117\%.$$

To determine the accuracy of the results yielded by this method, it was necessary to ascertain:

(1) Whether the gaseous compounds of phosphorus absorbed by sodium hypochlorite would be entirely

[1] *Z. Calc. Acet.*, **1**, 210 (1898).

taken up by two Friedrichs gas washing bottles containing the reagent, and

(2) Whether in the method here employed for the generation of the acetylene, any gaseous compounds of phosphorus are evolved that are not absorbed by sodium hypochlorite.

That complete absorption of the compounds of phosphorus is obtained with only two of the gas washing bottles of the type here described, even when a sample of carbide unusually high in phosphorus is used, was demonstrated by connecting four of the absorption bottles in series, charging each with 75 cc. of a 3 per cent. solution of sodium hypochlorite and testing the contents of each for phosphoric acid after the run. In no case was this acid detectable in the third or fourth bottle.

The second query was answered in two ways: The gases issuing from the second absorption bottle were burned with an excess of oxygen, and the products of combustion were found to be free from phosphoric acid. In another experiment, the crude acetylene from the generator was burned directly without being passed through the solution of sodium hypochlorite, and the result was found to agree with that obtained by the absorption method.

The combustion of acetylene as it issues from a bottle containing a liquid absorbent has heretofore presented difficulty because of the intermittent flow of the gas. It was found, however, that complete combustion is easily attained by passing the acetylene into the hydrogen inlet tube of a Linnemann oxy-hydrogen lamp, admitting oxygen into the other tube of the lamp, and insuring continuous combustion by causing a small horizontal flame, about 1 cm. long, of illuminating gas that is free from phosphorus to burn across the orifice of the lamp.

The accuracy and uniformity of the results obtained with the method here described are shown in the following tabulation of analyses by the absorption method, and by the method of combustion.

TABLE I.

This sample CaC_2 yielded 300 liters C_2H_2 per kilogram.

No.	Weight of sample in grams.	Weight of $Mg_2P_2O_7$ in grams.	Per cent. of phosphine in evolved acetylene: by NaClO method.	by combustion method.
1	50.3548	0.0089	0.0117	. .
2	50.3572	0.0073	0.0097	
3	50.1870	0.0062	0.0083	. .
4	50.3027	0.0050	0.0066	
5	50.0036	0.0062	0.0083	
6	50.3047	0.0059	0.0078	
7	50.1625	0.0059	0.0078	. .
8	50.0000	0.0072	. .	0.0096
9	50.0000	0.0047		0.0063
10	50.0000	0.0060		0.0080
11	50.0612	0.0062		0.0083
		Average	0.0086	0.0080

The results given in Table I were obtained with a sample of commercial calcium carbide. To ascertain whether the method would give uniform results when the acetylene contained a relatively large amount of phosphine, the authors prepared a sample of calcium carbide high in phosphorus, and the analyses of this product by the two methods are given in Table II.

TABLE II.

This sample CaC_2 yielded 287 liters C_2H_2 per kilogram.

No.	Weight of sample in grams.	Weight of $Mg_2P_2O_7$ in grams.	Per cent. of phosphine in evolved acetylene: by NaClO method.	by combustion method.
1	50.0651	0.0661	0.0925	. .
2	50.0200	0.0592	0.0829	.
3	50.0432	0.0782	0.1093	.
4	50.1004	0.0582	0.0814	. .
5	50.0600	0.0680	. . .	0.0948
6	50.1043	0.0641	. . .	0.0896
7	50.0612	0.0601	. . .	0.0841
8	50.0121	0.0642	. . .	0.0899
		Average,	0.0915	0.0896

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THE DETERMINATION OF LEAD SULPHATE AND THE ULTIMATE ESTIMATION OF SUBLIMED WHITE LEAD IN RUBBER.

By JOHN A. SCHAEFFER.

Received Aug. 9, 1912.

The extended use of sublimed white lead in the compounding of rubber and the gradual establishment of specifications regulating the content of sulphur allowable in certain grades of rubber, has brought forth the necessity of having some accurate and rapid method for the determination of lead sulphate in finished rubber.

Sublimed white lead as placed on the market is a basic sulphate of lead showing the following average percentage composition:

	Per cent.
Lead sulphate	78.5
Lead oxide	16.0
Zinc oxide	5.5

The lead sulphate and lead oxide are chemically combined as basic sulphate of lead and the compound consists of extremely fine, amorphous particles.

It is believed that the vulcanization of the rubber causes a decomposition of the sublimed white lead with the consequent formation of lead sulphide by union of sulphur with the lead oxide, which accounts in a measure for the remarkable results obtained when this compound is added to rubber. After the vulcanization the inert compounds, lead sulphate and lead sulphide, remain.

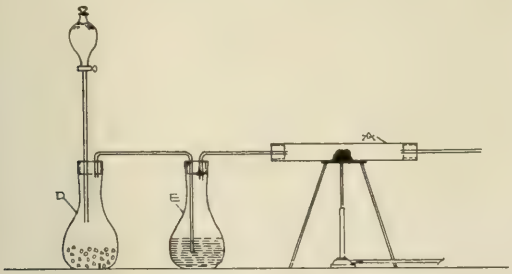
It is this property of rapid reaction, due to the extreme fineness of the particles, and the resultant formation of the inert compounds, which is causing the rapid increase in the use of sublimed white lead in the compounding of rubber.

Manufacturers, however, have restrained themselves from any extended use of the above compound in all grades of rubber which is sold under specifications, owing to the limited content of sulphur allowable, this sulphur being total sulphur regardless of whether the same is in an active or an inactive form. It has been known for some time that such specifications should not include sulphur which is present in an inactive form as is found in the case of the lead sulphate present through the addition of sublimed

white lead to rubber, provided some method for the differentiation of the active form from the inactive form be applicable.

Recent agitation on the above question led to work in our laboratory with the result that the following method was found to give accurate and rapid results for the determination of lead sulphate in finished rubber.

A two gram sample of the rubber under examination is placed in a hard glass tube, *A*, about one inch in diameter and about eight inches in length. The one end of this tube is connected to a carbon dioxide



generator, *D*, the carbon dioxide evolved passing through a bottle, *E*, containing water. The other end of the tube is closed with a stopper holding a small tube for the escape of the gas and decomposition products. Carbon dioxide is continuously generated by the action of hydrochloric acid on limestone.

After all the air in the apparatus has been replaced by carbon dioxide, the rubber in the hard glass tube is very gently heated until all the organic matter is driven off and the rubber has become a dry mass. Under these conditions all interfering organic matter is removed without the possibility of any oxidation of sulphur or sulphide to sulphate.

After complete decomposition, the tube is allowed to cool while carbon dioxide passes through the apparatus. The contents of the tube are then carefully and completely removed with a spatula, the hard mass being carefully ground in a small agate mortar and the finely ground residue placed in a small flask which is connected to the carbon dioxide generator in place of the hard glass tube. The powder in the flask is now treated with 25 cc. of concentrated hydrochloric acid.

The air is replaced by carbon dioxide and the contents of the flask gently boiled until all the sulphides are decomposed and any hydrogen sulphide evolved is driven off. This boiling will require from fifteen to twenty minutes. The decomposition of the mass by concentrated hydrochloric acid in the presence of carbon dioxide will remove any sulphides without chance of oxidation to sulphate and will dissolve practically all the lead sulphate.

After the sulphides are decomposed, the acid in the flask is diluted with water, the solution is filtered, and any residue is thoroughly washed with hot water. The residue remaining is ignited in a porcelain crucible, then digested with concentrated hydrochloric acid, the solution diluted, filtered, washed, and added to the original filtrate. It was found that from 0.1 to 0.2 of one per cent. of lead sulphate remained in the residue.

The greater portion of the free acid is neutralized with ammonium hydroxide and final neutralization is reached by the slow addition of sodium carbonate, after which about two grams in excess of sodium carbonate are added. The solution is boiled for fifteen minutes, filtered and thoroughly washed. By this process all the lead is removed as carbonate.

The sulphate present in the filtrate is precipitated with barium chloride, the usual conditions being observed. The sulphate is weighed as barium sulphate and calculated to sulphur and lead sulphate.

For the calculation of lead sulphate to sublimed white lead, the average composition of sublimed white lead is used, namely, divide the lead sulphate found by 78.5 per cent. This calculation must be made for determining the percentage of sublimed white lead present, as in no way can the original lead oxide in sublimed white lead be determined when once subjected to the process of vulcanization. However, as sublimed white lead varies but slightly in chemical composition, the result in this case will be quite accurate.

By the use of this method the following results were obtained on five different samples of rubber compounded with sublimed white lead according to various formulae:

Sample No. 1 was compounded with ceylon, sublimed white lead, litharge and sulphur. The percentage of sulphur added through the use of sublimed white lead was definitely known.

The analysis showed the following:

SAMPLE NO. 1.

Percentage of sulphur added by the use of sublimed white lead = 2.14.

Percentage of sulphur found present as lead sulphate.	Lead sulphate found.
2.31	21.92
2.19	20.74
2.25	21.31
2.25	21.31
2.17	20.54

Sample No. 2 was also compounded from ceylon, sublimed white lead, litharge and sulphur in widely different proportions from sample No. 1. The analysis showed the following concordant results on the percentage of sulphur present as lead sulphate.

SAMPLE NO. 2.

Percentage of sulphur found present as lead sulphate.	Lead sulphate found.
3.98	37 70
4.02	38.09
3.99	37.87

Sample No. 3 was compounded from sublimed white lead, zinc oxide, litharge and sulphur; the variety of rubber used, was, however, not submitted. The exact percentage of sulphur added through the use of the sublimed white lead was here again known. Six determinations gave very concordant results.

SAMPLE NO. 3.

Percentage of sulphur added by the use of sublimed white lead 1.36.

Percentage of sulphur found present as lead sulphate.	Lead sulphate found
1.42	13.45
1.41	13.40
1.36	12.89
1.46	13.83
1.46	13.86
1.41	13.39

Sample No. 4 was compounded with zinc oxide, sublimed white lead, litharge, and sulphur, though in different proportions from sample No. 3. The analysis showed the following:

SAMPLE NO. 4.

Percentage of sulphur found present as lead sulphate.	Lead sulphate found.
1.33	12.65
1.34	12.72
1.32	12.59

Sample No. 5 was a sample submitted for examination for the purpose of estimating the lead sulphate present. None of the other constituents were given. The concordance of the lead sulphate determinations was exceptionally good.

SAMPLE NO. 5.

Percentage of sulphur present as lead sulphate.	Lead sulphate found.
1.00	9.49
1.03	9.77
1.03	9.74
0.99	9.39

In order to determine whether there was any possibility of the oxidation of the lead sulphide, usually found in rubber, to lead sulphate during the decomposition, the following experiments were carried out.

Lead sulphide was freshly precipitated, filtered, thoroughly washed and dried. This was examined before using for lead sulphate. Two grams of sample No. 5 rubber were then thoroughly mixed with one gram of this lead sulphide and the decomposition was carried out in the usual way. The following results showed that no such oxidation had occurred:

Sulphur found in No. 5 as lead sulphate when decomposed in the usual manner. Three determinations	Sulphur found in No. 5 as sulphate, when mixed with freshly precipitated lead sulphide and decomposed in the usual manner. Two determinations.
3.98	4.03
4.02	4.06
3.99	
Lead sulphate found.	**Lead sulphate found.**
37.70	38.19
38.09	38.43
37.81	

Two samples of rubber which were compounded without the addition of sulphate in any form were then examined by this method of analysis, to still further determine whether there was any possibility of oxidation of sulphide to sulphate during the composition.

The samples were compounded according to different formulas, the one being made from ceylon, litharge and sulphur, and the other from zinc oxide and sulphur, the variety of rubber used, however, not being given.

A small percentage of sulphur present as sulphate was found in each case, but as the results on each sample were concordant, yet varied on the two samples, it is obvious that the danger of oxidation of sulphide to sulphate is slight, provided all the oxygen is removed from the apparatus by carbon dioxide before any decomposition is begun.

The results showed the following sulphur values on sample No. 6 compounded with ceylon, litharge and sulphur:

SAMPLE NO. 6.

Sulphur found as sulphate. Per cent.
0.145
0.148
0.171

Sample No. 7, compounded with zinc oxide and sulphur, showed the following:

SAMPLE NO. 7.

Sulphur present as sulphate. Per cent.
0.10
0.09

The slightly higher values for sulphur found present as lead sulphate in the samples examined where the content of sulphur present through the addition of sublimed white lead was definitely known may be due to this exceedingly slight oxidation of sulphide to sulphate, most probably during the process of vulcanization.

From the above results it will be seen that the percentage of sulphur present in rubber as lead sulphate can be accurately determined apart from the free sulphur and sulphide present in rubber. It will be noted that the sulphur present in the inert form as lead sulphate can be readily differentiated from other forms and eliminated in such cases where specifications call for a definite percentage of sulphur, by a determination of the sulphate in the above manner, and its subtraction from the total sulphur present. In accuracy and rapidity the method will be found to yield far better results than can be obtained by any of the other known methods for this determination.

Additional experiments are at present being begun toward the perfection of a method which will determine the percentage of lead sulphate present in rubber when compounded with sublimed white lead where other compounds such as calcium sulphate, calcium carbonate and barium sulphate are added. While this is purely an inorganic separation, it is hoped that a rapid method for such differentiation will be found. This paper serves as a preliminary one to a future paper in which this separation will be presented.

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THE EFFECT OF KILN-DRYING AT 145° F. ON THE COMPOSITION OF THE HOP.

By H. V. Tartar and B. Pilkington.

Received July 1, 1912.

The proper temperature to be used in the kiln-drying of hops is still a matter of dispute. In different parts of the world, we find temperatures varying from 70–150° F. recommended, the best authorities being widely at variance on the question. It is held that during the kiln-drying process at the higher temperatures a portion of the soft bitter resins, which give to the hop the major part of its real brewing value, are changed to a hard worthless resin, thereby causing a deterioration of quality. Remy[1] tried certain experiments as to the influence of kiln-drying on hops and his results showed that a considerable portion of the soft resin present in the fresh hop is converted into hard resin. The exact temperature at which these experiments were carried out, however, is not given. Gross[2] states: "Greater heat than 68–95° F. must not be used or the value of hops will be reduced, and for this reason the practice adopted, *e. g.*, in America, of drying at 140° F., cannot be recommended as worthy of imitation." Stockberger[3] says: "It is quite generally conceded that the so-called soft resin of the hop alone is valuable, the hard resin being worthless for brewing purposes. Yet the average grower knows nothing of these resins and frequently contrives to dry his hops at a temperature so high that a portion of the essential oil is volatilized and a considerable quantity of valuable soft resins is oxidized and converted into the hard, worthless form. In a series of recent experiments in the field, it has been shown conclusively that, within limits, the ratio of hard to soft resins varies directly with the temperature used in drying the hops." So far as the writer knows, the results of the experiments mentioned have never been published. Stockberger[4] also states: "The best temperature for drying is yet to be determined but every consideration indicates that it should be much lower than that commonly employed, probably between 100° and 140° F."

To the hop growers of the Pacific Coast the proper temperature to be used in kiln-drying is of vital importance. On account of the large size of many of the yards, in some cases amounting to hundreds of acres, the drying must be accomplished in a short time in order to handle the crop. Drying for several days at the low temperature of 70–90° F. as is done in some of the European countries, where the yards are small, cannot be employed without a practically prohibitory increase in the expense of drying. At the present time, the majority of the hop-growers of Oregon are using a temperature not exceeding 145° F.

Recent investigations made in this laboratory[5] have shown that the analytical methods which have been commonly used for the analysis of the hop are unreliable. The methods for the determination of the total soft resins and hard resin have been found to be very faulty. Since unreliable methods of analysis were evidently used for the examination of the hops in the kiln-drying experiments which have been reported, it was deemed advisable to repeat in a limited way, some of the work which had been done on the effect of kiln-drying on the composition of the hop, especially the effect of a temperature of 145° F.

[1] Chapman, "The Hop and Its Constituents," page 84.
[2] E. Gross, *Hops*, page 236.
[3] Address before American Brewing Institute, 1907.
[4] *Farmers' Bulletin* No. **304**, U. S. Dept. of Agr., page 24.
[5] This Journal, **4**, 209 (1912).

EXPERIMENTAL.

Samples were taken about the middle of September, 1910, at five different yards and in September, 1911, from two yards. Just as the hops, which had been picked in the usual manner, were being placed on the kiln a lot of hops, amounting to approximately 100 lbs. of fresh hops, was well mixed; a sample was taken and the exact spot in the kiln from which it was taken was carefully marked. This sample taken previous to kiln-drying was spread out and air-dried in the shade at room temperature. After the hops had been dried on the kiln, a second sample was taken from the identical spot where the first sample was taken, this second sample representing the hops after kiln-drying. The depth of the layer of hops on the kiln floor ranged from 22–30 inches and the length of time required for drying varied from 18–24 hours. The drying was continued in every instance until the stems or cores of the cones were well shriveled yet still soft and pliable, except in the case of samples 5*a* and 5*b* where the drying was continued until the stems or cores were somewhat brittle and easily broken. The kiln-dried samples were "sulfured" to the extent of about one-half lb. of sulfur per box of the fresh hops (50 lbs.). Great care was taken in handling the samples to avoid any loss due to the breaking of the cones and the sifting out of lupulin. The hops were all grown on sandy soil along the Willamette river with the exception of samples 4*a* and 4*b* which were grown on hill land.

The kiln dryers used at the different yards were, with one exception, ordinary "stove kilns" and were representative of those in common use. Samples 3*a* and 3*b* were dried on an "air blast" kiln in which air that had been passed over heated steam pipes was forced up through the hops from below by means of a "blast fan."

The temperature used in each instance ranged from 120–145° F. The drying was begun at the lower temperature and then gradually raised to 145°, at which temperature it was held as nearly as possible until the hops were dried. The temperature was taken with thermometers which were kept just under the floor of the kiln and at that portion of the kiln where the temperature was highest.

In making the analytical determinations the methods which have been worked out in this laboratory[1] for the determination of hard resin and total soft bitter resins were employed. The separation of the two soft bitter resins, the α and the β, was carried out according to the method outlined by Siller.[2] Chap-

[1] This Journal, **4**, 209 (1912).
[2] *Ztg. Untersuch. Nahrung-Genuss.*, **18**, 241.

man's[1] method was used for the determination of tannin. Moisture was estimated by drying *in vacuo* over sulfuric acid at room temperature. The determination of wax was made incident to securing the solutions necessary for the determination of the total resins The extract obtained by extracting the hops with ether was, after the evaporation of the ether, taken up with alcohol and the wax, which is insoluble in this solvent, was collected on a tared filter, thoroughly washed with alcohol, dried at room temperature and weighed. Owing to the small amount of volatile oil present and the consequent difficulty of making a quantitative estimation, the determination of this constituent was omitted and simply the physical examination made for aroma. Only whole, unbroken hop cones were used in making the analyses.

The results of the analyses are given in the accompanying table. In order to afford an accurate means of comparison, the amounts of wax, tannin and the different resins have been calculated to the dry matter.

The results indicate that there was little if any change in the composition of the hops during the kiln-drying process. It will be noted that excepting samples *2a* and *2b*, the amount of hard resin is slightly greater in the air-dried samples, a result which may be due to the variation in different samples. There was evidently little if any change in the amounts of tannin and wax, considering the possible variation in separate samples. A physical examination showed that the difference in the aroma of the air-dried and the kiln-dried samples was hardly perceptible, different judges varying somewhat in their opinions.

COMPOSITION OF HOPS, AIR-DRIED AT ROOM TEMPERATURE AND KILN-DRIED AT 145° FAHR.

		Composition of dry matter. Percentages.							
				Total soft	Hard	Soft resins.			
No.	Description of sample. 1910 crop.	Moisture.	Total resins.	bitter resins.	(gamma) resin.	Beta resin.	Alpha resin.	Tannin.	Wax.
1*a*	Kiln-dried from yard of T. A. Livesly, Salem, Ore.	5.14	20.11	18.22	1.89	11.18	7.04	2.50	0.31
1*b*	Air-dried, corresponding to 1*a*	6.42	21.09	19.02	2.07	11.53	7.49	2.55	0.26
2*a*	Kiln-dried from yard of H. Hirschberg, Independence, Ore.	4.33	20.92	19.32	1.60	12.02	7.30	2.31	0.44
2*b*	Air-dried, corresponding to 2*a*	4.65	20.27	18.72	1.55	12.84	5.88	1.98	0.49
3*a*	Kiln-dried, from yard of E. Clemens Horst, Independence, Ore.	4.41	19.33	18.56	0.77	12.98	5.58	1.83	0.48
3*b*	Air-dried, corresponding to 3*a*	5.72	19.82	18.84	0.98	12.50	6.34	2.42	0.43
4*a*	Kiln-dried from yard of F. S. Bradley, Banks, Ore.	5.44	17.37	16.35	1.02	11.73	5.64	2.13	0.40
4*b*	Air-dried, corresponding to 4*a*	4.75	16.51	15.16	1.35	10.51	6.00	1.97	0.39
5*a*	Kiln-dried, from yard of Krebs Bros., Independence, Ore.	5.60	19.40	17.62	1.78	12.12	5.50	2.36	0.47
5*b*	Air-dried, corresponding to 5*a*	4.80	19.36	17.27	2.09	11.11	6.16	2.60	0.47
	1911 crop.								
6*a*	Kiln-dried, from yard of H. Hirschberg, Independence, Ore.	5.60	10.08	17.57	1.51	11.73	5.84	3.60	0.45
6*b*	Air-dried, corresponding to 6*a*	4.85	19.45	17.49	1.96	11.06	6.43	3.64	0.45
7*a*	Kiln-dried, from yard of E. Clemens Horst, Independence, Ore.	5.85	20.59	19.17	1.42	13.59	5.58	2.76	0.44
7*b*	Air-dried, corresponding to 7*a*	7.00	20.62	19.00	1.62	13.53	5.47	3.14	0.44

CHEMICAL LABORATORY,
AGRICULTURAL EXPERIMENT STATION,
CORVALLIS, OREGON.

LABORATORY AND PLANT

COMBINATION OF THE CONTACT PROCESS WITH THE ORDINARY LEAD CHAMBER OR TOWER SYSTEMS; AN IMPROVEMENT IN THE MANUFACTURE OF SULPHURIC ACID.[2]

By WILLIAM WILKE.

Since the introduction of the Contact System as a practical method for making sulphuric acid, it has been usually regarded as simply a competitor of the older chamber or tower systems. It may be of interest to bring before you a system in which the Contact function is combined with the chamber system, giving a successful working method that shows economies and advantages not generally appreciated but very worthy of attention.

Sometime ago I was called upon to construct a chemical works which should be thoroughly equipped for the manufacture of mineral acids—the main problem involved being the construction of a plant wherein sulphuric acid of the various commercial grades and concentrations could be manufactured in the most economical way. My clients had already an installation of the Contact Process licensed under U. S. Patents of the Verein Chemischer Fabriken in Mannheim, for the production of strong acid, and the question arose whether we could economically and profitably reduce this highly concentrated acid to lower strengths.

In calculating the cost we had to take into consideration the license fee and other fixed charges, and it was found in the end that it was impossible to do this. There was, however, a market for Chamber acid; consequently it was thought possible to combine the Contact Process with the Chamber Process and attain the end in view.

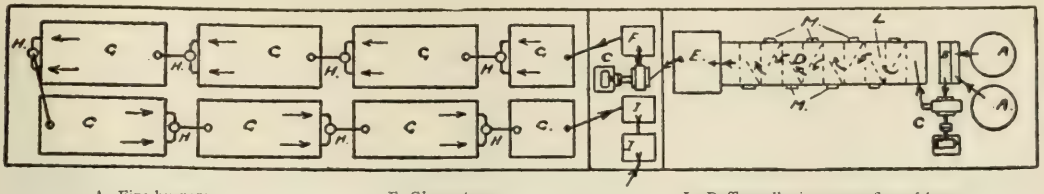
As a result of the study of conditions, a plant was designed as shown in the illustration. In order to be independent of the constant variations in the pyrites market and the possible scarcity of pyrite fines, the plant was so designed that lump ore as well as fines could be roasted, the burning capacity finally adopted being 24,000 lbs. fines and 36,000 lbs. lump ore. Thirty-six lump burners were installed, each able to handle from 900 to 1200 lbs. ore daily, and four standard Herreshoff fines burners.

The gases from the fines burners were conducted into a flue situated above the flue of the lump burners and provided with a number of baffle walls to

[1] *Jour. of Inst. of Brewing*, **13**, 646 (1907).

[2] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

catch some of the dust. The gases of the lump burners and fines burners were united and conducted into the patented iron-oxide-contact-shaft, similar to the contact process chamber of the Verein Chemischer Fabriken. In order to regulate the draft on the fines burners, a separate exhaust fan was installed to draw



A. Fine burners.
B. Small dust chamber.
C. Exhausters with electric motors.
D. Lump burners.
E. Iron-oxide-contact-shaft.
F. Glover tower.
G. Chambers.
H. Intermediate towers.
I. Gay-Lussac towers.
K. Exit from Gay-Lussac tower.
L. Baffle-walls in upper flue of lump burners.
M. Cleaning doors in upper flue of lump burners.

the gases from the fines burners and deliver them into the flue over the lump burners. A second exhaust fan was installed between the iron-oxide-contact-shaft and the Glover tower, which took the sulphurous gases after they had undergone conversion, to the extent of 30 per cent., into SO_3 by the iron-oxide-contact-shaft and forced them through the Glover tower into the chamber system.

The combination of the two very distinct processes into one system gave most excellent results. It was found that:

1. The capacity of the chamber plant was increased at least 30 per cent.

2. The conversion of SO_2 to SO_3 in the iron-oxide-contact-shaft averaged about 30 per cent.

3. At the same time the acid produced in the Glover tower was water-white.

4. The iron oxide eliminated 95 per cent. of the arsenic carried by the gases leaving the roasters and flues.

Finally it was proved that the total production of the chamber system could easily be concentrated to 60° Baumé or higher in the Glover tower.

Such satisfactory results are all attributable to the introduction of the iron-oxide-contact-shaft between the burners and the Glover tower; in other words, to the suitable combination of the contact and the lead chamber processes.

The iron-oxide-contact-shaft retards the dust and is the best known means of keeping dust from getting into the chamber system; it is an accumulator of heat and acts as an equalizer on any system, such as that described, enabling the operator of the plant to carry out the process more uniformly; it saves 30 per cent. of the niter consumed in the ordinary plant, on account of the conversion of the catalytic action.

Since constructing the above described plant, the iron-oxide-contact-shaft has been introduced in other existing chamber plants with equally good results.

BUFFALO, NEW YORK.

A SIMPLE TEST FOR THE DETERMINATION OF BUTTER-FAT IN BUTTER.

By JAMES M. DORAN.

Received August 15, 1912.

At the present time, owing to the federal and the various state laws fixing a standard for butter-fat in both creamery and renovated-butter, there is a demand for a simple field test, such as might be used in any creamery or by any state or federal officer engaged in the inspection of butter.

The following test is not to be considered as taking the place of the chemical method of determining butter-fat in butter, but merely as a control test or to be used by an officer in a preliminary examination.

It has several advantages that commend it as a field test:

1. The apparatus is cheap and simple and may be purchased from any supply house.

2. It is portable.

3. There is no weighing of sample.

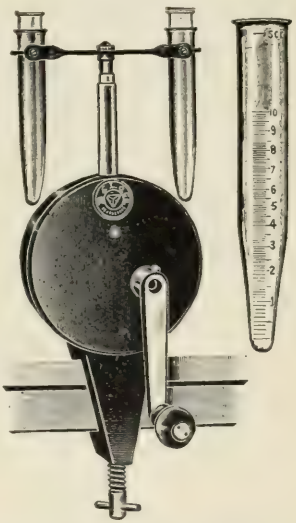
4. The only reagent used, gasoline, can be obtained sufficiently pure practically everywhere and at little expense.

The outfit consists of:

1. A simple hand centrifuge such as is used in urine analysis or milk analysis. It can be clamped to any table or support.

2. Several accurately graduated 15 cc. sedimentation tubes.

3. Some gasoline of good quality.



HAND CENTRIFUGE, SINGLE SPEED (1/4 ACTUAL SIZE) AND SEDIMENTATION TUBE.

The procedure is as follows: The sample of butter, taken with a trier or otherwise, is first warmed to about 100° F. and thoroughly stirred to insure the mass being uniform. About 10 cc. of the sample is placed in the sedimentation tube and whirled in the centrifuge for a few seconds. The sample should be sufficiently liquid in order to insure a good reading after being whirled in the centrifuge. After reading the amount of the sample on the tube scale, about 5 cc. of gasoline is added and the tube carefully inverted two or three times, holding the thumb or finger over the top of the tube. Let the solution of fat and gasoline drain a few seconds before removing the finger.

Place the tube in the centrifuge and whirl again for 15 or 20 seconds.

The gasoline dissolves the fat, forming a clear layer on the top. The non-fats, that is the water, salt and curd, being immiscible with the gasoline and also heavier, form the lower layer. The second whirling drives the non-fats to the lower end of the tube almost completely, at the same time forming a sharp line of division between the two layers. The amount of non-fats is then carefully read on the tube scale.

The following is an example of the calculation of the butter fat from these two readings:

	Cc.
Total sample	9.8
Non-fats	1.7

$$\frac{1.7 \times 100}{9.8} = 17.36 \text{ per cent. non-fats.}$$

$100 - 17.36 = 82.64$ per cent. butter-fats.

Care should be taken that this test is made at a fairly uniform temperature in order to eliminate as far as possible the changes in relative volumes due to variations in temperature.

In case the sample when first placed in the sedimentation tube is not sufficiently liquid to insure a good reading on being whirled, it may be warmed by placing it in water or in an oven for a few minutes at a temperature not over 110° F.

The results of many tests by this method show a variation of not over 0.2 per cent. fat on the same sample, and within the limits of about 0.5 per cent. fat when compared with the official method.

TABLE OF COMPARATIVE RESULTS ON PERCENTAGE OF BUTTER-FAT OBTAINED BY USE OF CENTRIFUGAL METHOD AND OFFICIAL CHEMICAL METHOD.

	Percentage butter-fat.		
Sample No.	Official method.	Centrifugal method.	Percentage difference.
38277	78.68	79.12	0.44
38281	79.81	80.30	0.49
38283	78.06	78.56	0.50

BUREAU OF INTERNAL REVENUE,
WASHINGTON.

APPARATUS AND METHOD FOR SULPHUR DETERMINATION IN PETROLEUM ILLUMINATING AND LUBRICATING OILS.[1]

By P. H. CONRADSON.[2]

The methods generally used in determining sulphur in petroleum, illuminating and lubricating oils do not give either the total amount of sulphur compounds present or how they occur. The writer has found that in many inferior, poorly refined petroleum oils large percentages of the total sulphur compounds present may be due to sulphonates or sulphates, which altogether escape notice in the so-called lamp methods where the oil is only partly consumed in the lamp, while in the direct oxidation methods no distinction is made.

In the examination of the illuminating (kerosene) oils used in railroad service, such as in locomotive headlights or track signal lamps (long time burner lamps) which latter require an oil with hardly any diminution in the intensity of light or candle power for 175–250 hours continuous burning with no attention, or lubricating oils, such as are used in steam turbines, gas or oil engines, superheated steam valve and cylinder lubrication, high pressure air compressors or high vacuum air pumps, it is essential to differentiate between the sulphur compounds that might be present in the oils; therefore, the writer has found it necessary not only to burn a larger amount of oil in the lamps, but also to consume all the oil in the oil fount and make a careful examination of the sulphur compounds that may remain in the wick.

The accompanying photographic cut of the apparatus[1] is self-explanatory—using ordinary small kerosene burners with chimneys, well washed and dried cotton wicks about 3 mm. ($^1/_8$″) in width. The lamp founts for the *illuminating* oils are ordinary glass beakers; for the *lubricating* oils, funnels having the stems cut off and fastened to a metal socket. The burners are inserted in a small disk (lid of an ointment box with a hole cut to fit the burner). Filter tubes of strong glass with stem bent at right angles are fit snugly over the long arm of the glass stoppered absorption tubes, which are about 350 mm. (14″) in length between the constriction and exit tube and have a diameter of about 25–35 mm. (1″–$1^1/_4$″) and contain small glass beads to a depth of about 80 mm. (3″).

The products of combustion are aspirated through carbonate of soda solution containing 6 grams of Na_2CO_3 in one liter of water and standardized with $^1/_{10}$ normal hydrochloric or sulphuric acid. In testing, place 25–50 cc. of the soda solution in the first absorption tube; at the end of the operation the soda solution is run into a beaker and the chimneys, glass filter tubes and absorption tubes are rinsed out with water; the solution with the washings is titrated, using methyl orange as an indicator; or, the solution may be oxidized with bromine and hydrochloric acid, precipitated with barium chlorid solution in the usual way and calculated to sulphur (S). The wicks are separately treated and examined for sulphur compounds that may remain in the same from the oil, as will be described hereafter.

ILLUMINATING OILS.

For low-sulphur oils such as kerosenes made from Pennsylvania crudes, 15–20 grams of oil are used.

For kerosenes made from western crudes containing larger percentages of sulphur compounds, 10–15 grams are used.

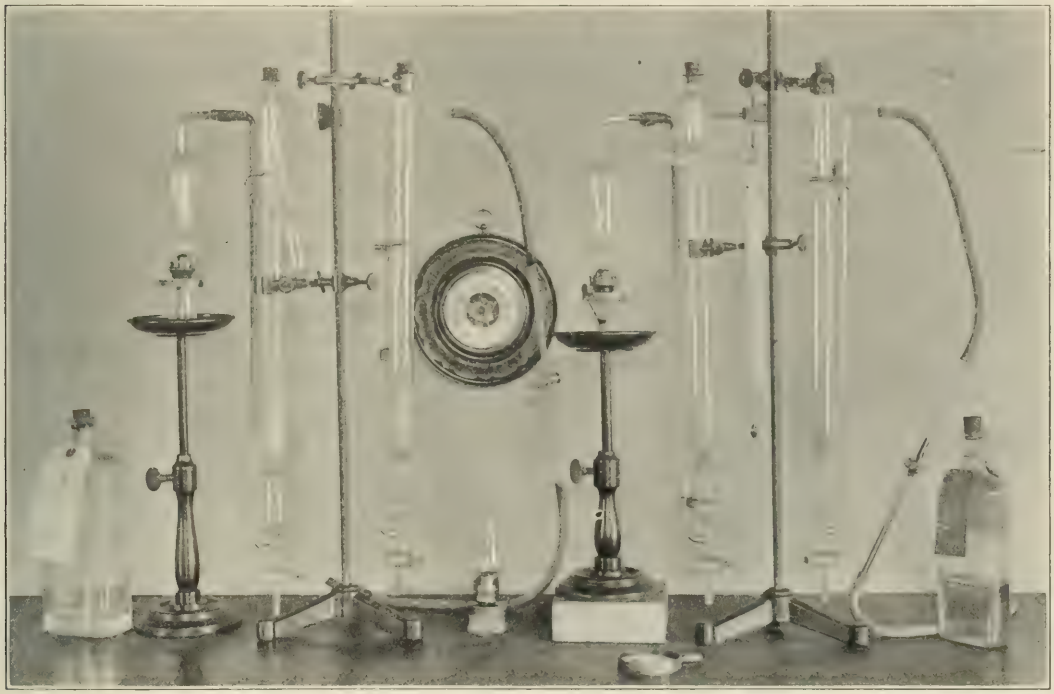
For kerosene oils intended for severe railroad service either for headlight oil purposes or in long-time burner signal lamps, it is well to make two sulphur determinations, one as above indicated and the other as follows: 425 cc. of the oil are carefully distilled in a 600 cc. Engler's distilling flask at the rate of 2–4 cc. per minute (the slower rate at the beginning and at the end), until 400 cc. have come over; the Engler's flask is placed on an asbestos gauze and covered over with asbestos wool up to the top of the neck, the ther-

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

[2] Chief Chemist, Galena-Signal Oil Co.

[1] In the cut the second absorption tube of the apparatus to the right is wrongly connected.

mometer bulb placed opposite the exit tube as usual. The 25 cc. residue in the distilling flask is transferred to a bottle. Often with ordinary or poorly refined kerosene oils there is formed a deposit or sediment, more or less adhering to the sides and bottom of the flask; it should be carefully removed and added to the residue in the bottle by using successively ethyl ether, chloroform, 95 per cent. ethyl alcohol and hot water (as the case may require), uniting and evaporating the solvents in a small dish and transferring the final residue to the bottle by the aid of some of the 25 cc. oil residue. The sulphur compounds are then



determined by burning the whole or part of the above well mixed oil residue to dryness in the apparatus above described.

LUBRICATING OILS.

Five to 10 grams of lubricating oils are burned to dryness in the lamps as stated with kerosene. Spindle oils, thin turbine oils and automobile oils will feed through the wicks until they are all consumed, with possible once or twice trimming of the formed crust; with thick, high-viscosity oils, 5–8 cc. of highly refined low-sulphur kerosene are added and the mixture burned to dryness or practically so; then 2 cc. more of the kerosene oil are added and burned to dryness.

The soda solution and washings are treated as above described, deducting for the sulphur in the 5–10 cc. of added kerosene.

The wicks from the above described lamp tests are treated as follows: Cut same in small pieces, transfer to a 50 cc. porcelain crucible, add 0.2 gram pure dried carbonate of soda and 5 cc. 1.42 sp. gr. nitric acid, digest on steam or water bath (cover crucible with inverted lid) till the fibers are disintegrated; then add 2 grams pure crystallized magnesium nitrate; continue the digestion, gradually raising the temperature on hot plate or protected gas flame till the organic matter is destroyed and most of the nitrates decomposed, leaving a white residue; after cooling add sufficient bromine water and hydrochloric acid, boil, dilute and precipitate with barium chlorid in the usual way and calculate to sulphuric acid (SO_3). This includes the SO_3 both in form of sulphates and sulphonates if both are present. If it is desired to estimate the latter separately, boil the wicks with 10–15 cc. strong barium hydrate solution; dilute to 100 cc. with boiling water; filter and wash. The filtrate is either oxidized with bromine and hydrochloric acid or evaporated with a few drops of nitric acid to dryness and slightly ignited, the residue being treated with hydrochloric acid and boiling water. The insoluble $BaSO_4$ in either case is calculated to SO_3 in sulphonates. The remaining wicks with any insoluble barium salts are then oxidized with nitric acid and magnesium nitrate, the residue taken by boiling with bromine water and hydrochloric acid; the insoluble, if any (barium sulphates), is calculated to SO_3 present in the oil as sulphates.

The usual precaution of making blank tests with the chemicals or reagents and wicks should not be omitted.

A few analyses by the above methods are given in the following table:

ILLUMINATING OILS

		Sulphur in lamp calculated to S. Per cent.	Sulphur compounds in wick from sulphonates and sulphates calculated to SO_3
1	Kerosene original	0.015	No SO_3
2	Kerosene original	0.035	Trace SO_3
2a	Kerosene in 25 cc. residue	0.038	Trace SO_3
3	Kerosene original	0.071	0.0075 per cent.
3a	Kerosene in 25 cc. residue	0.135	0.013
4	Kerosene original	0.018	None
4a	Kerosene in 25 cc. residue	0.057	None

LUBRICATING OILS.

1	Turbine oil	0.035	None
2	Turbine oil	0.098	0.098 per cent.
3	Engine oil	0.354	0.018 per cent.
4	Machinery oil	0.345	0.032 per cent.
5	Heavy gas engine oil	0.080	0.074 per cent.

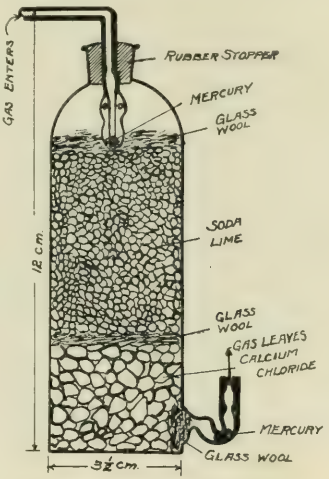
GALENA SIGNAL OIL COMPANY,
FRANKLIN, PA.

CARBON DIOXIDE ABSORPTION BOTTLE.

By W. A. KOENIG.

Received April 10, 1912.

Fig. 1 represents a piece of apparatus that is a great time-saver in making determinations of carbon in steel drillings. It consists of a round bottle having a mercury trap at both the inlet and outlet; these make it possible to weigh the bulb without removing the oxygen.



CO_2 ABSORPTION BOTTLE

The bottle is filled, as shown, with calcium chloride and dry soda lime; the traps with a very little freshly distilled mercury. When filled, it weighs between fifty and sixty grams and lasts for at least one hundred determinations where the carbon content is about one per cent.

The apparatus is so simple in construction that any fairly good glassblower could make it.

MIDVALE STEEL CO.,
PHILADELPHIA.

A NEW ALLOY WITH ACID RESISTING PROPERTIES.[1]

By S. W. PARR.

While marked advances have been made in the development of alloys with properties which render them resistant to the corroding influence of the atmosphere, not so much study has been given to the production of alloys which would resist the solvent action of strong chemicals. This latter function of resistance to chemical action has been given over almost wholly to the noble metals. However, there are certain specific requirements such as ordinarily call for the use of gold or platinum where the quantity of metal involved and the excessive cost of the same make its use almost prohibitive. These considerations have led to the studies herein described in which the effort has been made to develop an alloy especially resistant to nitric and sulphuric acids.

A preliminary study was first made of certain of the more common alloys with a view to determining their relative solubility in nitric acid. An arbitrary strength of acid was chosen which was obtained by diluting the ordinary strong acid of 1.42 sp. gr. in the ratio of 1 of acid to 3 of water, making approximately a 25 per cent. or $4N$ solution of HNO_3. The alloys employed, together with their order of solubility, is shown in Table I.

TABLE I.—RELATIVE SOLUBILITY OF METALS AND ALLOYS IN 25 PER CENT. NITRIC ACID.

		Percentage dissolved in 24 hours.
1	Pure iron 99.8% pure	100.0
2	Commercial aluminum	51.4
3	Monel metal	19.2
4	Nichrome, Ni 90, Cr 10	7.9
5	Copper aluminum, Cu 90, Al 10	3.5
6	Nickel (79), chrome (20), aluminum (1)	1.3
7	Ferro silicon	0.1

The tests in Table I were based on the per cent. dissolved in 24 hours at room temperature. They are of value only as they show relative solubilities. Test pieces were used of approximately the same superficial area. The amounts dissolved expressed as percentages are sufficiently accurate for comparison. The range of solubilities varies widely, being from 100.0 to 0.1 per cent.

The last two items on the list suggest the possibility of carrying the series further. Because of its physical characteristics of brittleness, lack of working qualities, etc., the last number, ferrosilicon, was not selected as affording an encouraging basis for experimentation. The next to the last number however, the nickel chrome compound with a small amount of aluminum, was selected as a suitable type for further study. A series of six mixtures was arranged as in Table II wherein it was sought to determine the effect of the introduction of copper. Some such modifying element seemed necessary for the reason that the value of No. 6 in Table I was nullified to a large extent by reason of the difficulty experienced in casting that material free from flaws. The melting point of the mixture was extremely high, approximately 1500°, and it was thought that by the introduction of a metal of lower melting point a product would be obtained which would flow more freely and solidify without blow-holes. The series arranged, therefore, was a nickel-copper-chrome combination with decreasing amounts of copper and increasing percentages of chromium as shown in Table II.

TABLE II.

Series No.	1.	2.	3.	4.	5.	6.
Parts Ni	65	80	80	80	75	70
Parts Cu	30	10	5	5	5	10
Parts Cr	5	10	10	15	20	20
Soluble in 25 per cent. HNO_3—24 hours	easily soluble	1.25 per cent.	0.02 per cent.	0.05 per cent.	0.013 per cent.	0.023 per cent.

The interesting fact developed in this series was the

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

degree of resistance that could be attained with considerable quantities of copper present. Nos. 3 and 6 were substantially of the same resistivity but No. 3 was more sluggish in pouring. Very little difference could be detected between Nos. 5 and 6, hence the latter was taken as a basis for further experiments. It was evident from the impossibility of securing perfect cast material from No. 6 that a study must be made of purging agents to clear the bath of oxides and dissolved gases. Aluminum could be used to advantage in this regard while at the same time the resistance to the acids was slightly increased. Tungsten was a slight further aid and manganese up to an amount equaling 1 per cent. did not appreciably augment the solubility factor. Other deoxidizers and denitrifiers in various forms were used, such as boron, silicon, titanium and vanadium—the effect of the last one, seemingly, to increase the solubility. The others in fractional percentages were effective both in improving the resistivity and the texture as well. The average range of values employed was approximately as follows:

TABLE III.—SHOWING COMPOSITION OF ACID RESISTANT ALLOY

Ni	66.6
Cr	18.0
Cu	8.5
W	3.3
Al	2.0
Mn	1.0
Ti	0.2
B	0.2
Si	0.2
	100.0

Not all of the difficulties of casting the material have been eliminated by any means. In proportion as the texture and soundness have been improved upon, the difficulties connected with casting the material have increased. The contraction of the metal at the moment of solidification is very pronounced and shrinkage cracks are very likely to occur. However, these difficulties are chiefly physical and mechanical and in each specific condition they can doubtless be finally overcome. The alloy draws into wire and spins readily and may have numerous interesting applications.

As a method for more precisely measuring the acid resistance of the material, test pieces were prepared having an easily determined superficial area. These pieces were subjected to $4N$ HNO_3 and in mixtures of nitric and sulphuric acids of similar concentration, for 24 hours at room temperature. The loss in weight was calculated to a unit area of 100 sq. cm. per hour. The comparative values are given in Table IV.

The various melts differed slightly in composition, the attempt being made to determine the limits of certain ingredients, especially manganese, copper and aluminum. The best results were obtained with compositions conforming most nearly to the values given in Table III. The solubility in sulphuric acid was found to be as a rule no greater than in nitric acid, hence, the solubility tests were made on mixtures of the two instead of upon the sulphuric acid alone.

Very few tests on hydrochloric acid were made. As a rule the solubility of this type of alloy is considerably

TABLE IV.—SHOWING LOSS IN MILLIGRAMS PER 100 SQ. CM. PER HOUR.

NUMBER OF MELT.	$4N HNO_3$. mg.	$4N H_2SO_4$ mg.	$4N HCl$. mg.	1 vol. $4N HNO_3$. 2 vol. $4N H_2SO_4$. mg.
23	0.03			1.95
	0.03	0.79	1.95	1.98
	0.50			
	0.06			
25	0.19			0.0
	0.08			0.17
40	0.4		1.10	0.09
	0.3		1.30	0.10
				1.00
54	0.3		3.70	0.8
60	0.2		1.95	4.8
	0.4		2.05	5.2
64	2.0		2.70	0.3
	1.85			0.2

greater in hydrochloric acid than in nitric or sulphuric acids.[1] Indeed, a study of the various properties of the material up to the present time has been preliminary and largely qualitative. The detailed examination on structure, solubilities, physical and electrolytic properties has been deferred until a practicable or workable alloy could be obtained. This has now been accomplished in a very satisfactory manner and further work as above indicated will be continued. As illustrating the practical value of the alloy a calorimeter bomb was constructed and has already served for heat determinations upon an extended series consisting of sugar, benzoic acid, ethyl-benzene and coals. The pressures employed have ranged from 25–50 atmospheres and charges of material up to $1^1/_2$ grams have been used. The results are all that could be desired. An illustration of the cap or cover to the bomb was given in my article published in THIS JOURNAL, page 746. The interior surface which comes in contact with the corroding gases retains its polish and luster without any evidence of chemical action. The details of the behavior of the alloy in this apparatus were given in a paper entitled "Some Tests on a New Calorimeter Bomb," by Dr. R. H. Jesse, Jr., THIS JOURNAL, page 748.

UNIVERSITY OF ILLINOIS,
URBANA.

[1] "Stellite," a cobalt-chrome alloy described by E. Haynes, THIS JOURNAL **2**, 397 (1910), shows a solubility under the same conditions of 17 milligrams per 100 sq. cm.

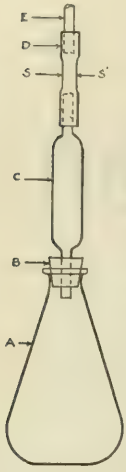
MODIFIED BUNSEN VALVE.

By LESLIE RUSSELL MILFORD.

Received August 12, 1912.

In making analyses of total iron, the following scheme has been adopted by the author in working on the Saratoga Mineral Waters. When reducing the ferric compounds to ferrous, by means of nascent hydrogen, an Erlenmeyer flask with a Bunsen valve attachment has been used. The accompanying cut shows at a glance the modification which has been satisfactory.

A, Erlenmeyer flask.
B, Cork.
C, Bulb cut from 10 cc. pipette.
D, Rubber tubing.
E, Glass plug.
SS′, Slits for valve.



Instead of an ordinary straight piece of glass tubing a bulb, C, from a discarded 10 cc. pipette is used, one end of which is inserted into the cork B, projecting just below the surface into the Erlenmeyer flask A; to the other end is joined a piece of rubber tubing, D, carrying a glass plug, E.

The ferric solution to be reduced is put into the Erlenmeyer flask, dilute sulphuric acid and zinc dust are added and the flask is then placed on the steam bath. The nascent hydrogen produced by the action of the acid on the zinc reduces the iron rapidly. When all of the zinc is in solution the flask is taken from the bath, placed on a wire gauze and the contents are brought to boiling so as to eliminate any hydrogen in the flask as this would decompose the $KMnO_4$ solution when added. It is at this point that the improved valve works to advantage. The steam in escaping expands in the 10 cc. bulb, condenses and runs back into the flask. This eliminates the excess pressure and blowing out of the stopper. After thorough boiling, the flask is taken from the gauze, the stopper removed, the sides washed down, and a very little c. p. $NaHCO_3$ is dropped into the flask to generate an atmosphere of CO_2. The solution is then titrated with standard $KMnO_4$.

STATE HYGIENIC LABORATORY,
ALBANY, N. Y.

A SIMPLE FORM OF LABORATORY SUPPORT.

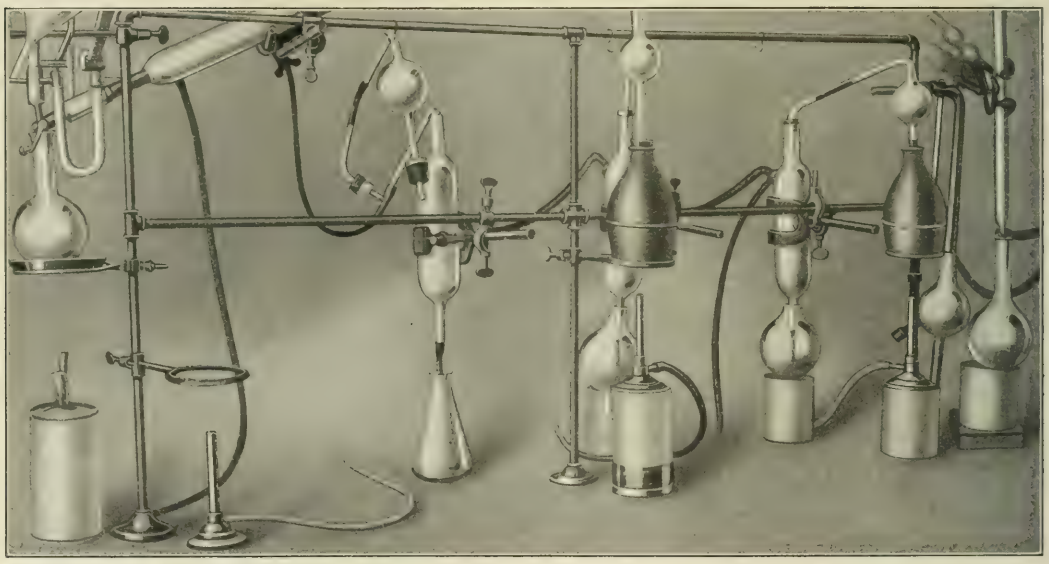
By T. LINSEY CROSSLEY.

Received August 21, 1912.

The accompanying illustration shows a form of support for apparatus which has been found very useful in this laboratory.

It consists of $^3/_8$ inch rod and pipe fittings. The footing pieces are screwed into round plates and fastened to the bench. The size of rod is such as to suit the usual retort stand fittings. It has the advantages of lightness, firmness, adaptability, and cheapness. It does away with the heavy undergrowth of retort stand footing.

Any pipe fitter can make such apparatus very quickly. Other forms and uses will readily suggest themselves. The apparatus shown is carrying three vertical condensers and apparatus for Kjeldahl distillations, a Liebig condenser and a Jones reductor, with space for other work, taking the place of five retort stands and several tripods with their accompanying risk of breakage.



MONTREAL, QUEBEC.

OBITUARIES

MORRIS LOEB.[1]

Morris Loeb, President of the Chemists' Club of New York City, died at Seabright, New Jersey, October 8, 1912, from typhoid fever and double pneumonia, after an illness of eighteen days. He was born in Cincinnati, Ohio, May 23, 1863.

Morris Loeb was a man in speaking of whom I wish I might have had time to choose my words with more deliberation. His nature showed itself always in such a refinement as to command its tracing only with the most delicate touch. Tender

[1] Presented at the October meeting of the New York Section of the American Chemical Society.

is the wound in losing a friend in science whom I had known for nearly twenty years—in fact, since the time he was the Secretary of the Section of Chemistry of the American Association at the Brooklyn meeting. At that time he was participating in the great task of habilitating the American Chemical Society, with the history of which no doubt all here are familiar.

I wish I were able to fittingly tell you of the spirit actuating him at that time, as it proved an inspiration to me then, and afterwards served to cement a friendship into a closer personal relationship.

Born and reared in wealth, a great plan in the business world ready for his acceptance, while gaining a broad culture at Harvard, he inhaled the breath of Wolcott Gibbs' scientific spirit, which carried him to Hofmann at Berlin. Three papers were published by him while at Berlin, the last being his dissertation.[1] All dealt with carbonyl chloride and its conduct with various amidines. This work was interesting and possessed that normal importance to the candidate for a degree: but Loeb was not satisfied. That was in 1887. The roving ardor of an awakening of physical chemistry was in the air. It carried him to Heidelberg and then to Leipzig to be with Ostwald, who had just made Arrhenius a real power.

By the advice of Ostwald, Loeb undertook to study the molecular weight of iodine in its solutions by the vapor-tension method.[2] His experimental results led him to conclude: "It seems very probable that iodine in its red solutions has a molecular weight corresponding to I_4, while in the violet solution in carbon disulphide there is a less complex aggregation, giving a value between I_2 and I_3." He found that the method of determining molecular weights by the depression of the freezing point is preferable to the method by vapor tensions. He lacked a liquid which would solidify and also dissolve iodine with a pure violet color; but he endeavored to obtain what corroborative evidence he could by experimenting on the freezing points of iodine in acetic acid and in benzene, although he was eventually forced to give up the attempt by the very slight solubility of iodine in these menstrua at low temperatures. The molecular weight of iodine as calculated from various series of observations seemed to increase continuously with the concentration, so that there was no point in the narrow limits between extreme dilution and saturation at which the molecular weight would appear constant and could be accepted as trustworthy. This was later confirmed by Paterno and Nasini.[1]

MORRIS LOEB.

With the intention of testing the then latest views on electrolysis, work in which field he had begun with Gibbs, while still at Leipzig, Loeb, with Nernst, carried on a study of the kinetics of substances in solution.[2] From determinations of Hittorf's ratios of transference and the conductivity of a number of silver salts, they calculated the ionic velocity of silver, according to the principles laid down by Kohlrausch. The constancy of the value obtained from observations with eight different salts gave satisfactory evidence for the truth of the theory, the numbers varying only within very narrow limits. Loeb and Nernst also gave the calculated values for the velocities of the other ions, and it further appeared from a comparison with the temperature coefficients of the velocities that they decrease as the velocity increases.[3]

Loeb then felt ready to come back to the master who had changed his course in life and to tell him what they were doing in Europe. So in 1888–9 he returned as voluntary assistant to Gibbs, who had retired from Cambridge to his private laboratory at Newport. After a year, Gibbs realized Loeb's power as a teacher and made him go to Clark University as docent in chemistry.

In a report on "Osmotic Pressure and the Determination of Molecular Weights,"[4] Loeb discussed Raoult's law, the matured papers of van't Hoff on osmotic pressure, the measurement of osmotic pressure, and the methods of determining the molecular weight from the vapor tension. At this time (1890) experimental data to show the value of Beckmann's method had not been published, but Loeb predicted that it would play as great a part as the freezing point method introduced in its most convenient form by the same chemist.

Shortly afterwards, in a review, Loeb sketched Arrhenius' hypothesis, with some of its logical consequences.[5] He discussed the physical and chemical objections known in 1890, leaving "the task of judging it . . . to those readers who will compare the mass of experimental material and will convince themselves

[1] These papers were "Ueber die Einwirkung von Phosgen auf Aethenyldiphenyldiamin," *Ber.*, **18**, 2427 (1885); "Ueber Amidinderivate," *Ibid.*, **19**, 2340 (1886); "Das Phosgen und seine Abkömmlinge, nebst einigen Beiträgen zu deren Kenntnis," Inaug. Diss., 15 März, I. Chem. Labor d. Berlin Univ., *Chem. Zentr.*, **58**, 635–1887.

[2] "Euber den Molekularzustand des gelosten Jods," *Z. physik. Chem.*, **2**, 606. "The Molecular Weight of Iodine in Its Solutions," *Trans. Chem. Soc.*, **53**, 805.

[1] *Ber.*, **21**, 2153

[2] "Zur Kinetik der in Lösung befindlichen Korper. Zweite Abhandlung. Ueberführungszahlen und Leitvermögen einiger Silbersalze von Morris Loeb and W. Nernst," *Z. physik. Chem.*, **2**, 948.

[3] Loeb also published in this year a paper on the "Use of Aniline as an Absorbent of Cyanogen in Gas Analysis," *Trans. Chem. Soc.*, **53**, 812 (1888).

[4] *Am. Chem. J.*, **12**, 130–5.

[5] "The Electrolytic Dissociation—Hypothesis of Svante Arrhenius," *Ibid.*, **12**, 506–16.

of the simple relations which the various phenomena appear to bear toward each other. As far as this test is concerned, Loeb maintained, "the hypothesis will be found to fulfil its purposes."

In the exact measurement of electric currents, employing the method wherein the determination of the amount of silver deposited from a neutral solution of a silver salt is made, the source of error, particularly where weak currents are concerned, arises from the imperfect adhesion of the silver upon the cathode. The latter is generally a platinum crucible, and Loeb[1] found that a Gooch crucible with asbestos felting over the holes was a far better form of cathode, providing an arrangement was adapted to hold the solution during electrolysis without leaking. He attained this very satisfactorily by replacing the ordinary platinum cap with a glass siphon of special form.

Then, when but twenty-eight years of age, he was called to the Chair of Chemistry at New York University. He published a paper entitled "Apparatus for the Delineation of Curved Surfaces, in Illustration of the Properties of Gases, etc."[2]

Professor Loeb thought that, just as an electric system is affected by its approach to or removal from a magnetic field, a reaction which made a system more or less amenable to magnetic action might show evidence of acceleration or retardation by the magnetic force. He concluded that if this effect were appreciable, the relation between magnetic force and affinity would be established, and data could be obtained for calculating the real value of magnetization. His experimental results, however, were negative, and he was led to believe that no such relation exists, unless it was so slight that his means of observation were inadequate.[3]

It was shortly after this that I met Morris Loeb. He was fired with the zeal of those captain teachers and his own lighted torch he passed on by students of his who now reflect in many responsible positions that spirit of the eighties.

Soon the very heavy responsibilities of a large inheritance fell upon him. Filial duty of meeting those responsibilities, professorial obligations, and research aspirations required the sacrifice of one of the three. The last was sacrificed for a dozen years. The irksome strain of being "by bells directed" began to tell, for to meet them he found it necessary to have his secretary travel with him. One morning he asked me to go with him to the University. We talked things over and he said he would have to give up the professorship, but would equip a private laboratory in the old Chemists' Club, where he would be nearer his philanthropic obligations and might do some research, and "*other things*" perhaps as useful to chemistry as teaching.

In 1905 he published a research on "The Crystallization of Sodium Iodide from Alcohols."[4] He found that apparently the molecular proportion of alcohol assimilated by sodium iodide decreases as the series ascends. The addition products determined were: $NaI.3CH_4O$, $NaI.C_2H_6O$, and $5NaI.3C_2H_6O$.

In 1908, ever keeping abreast with the advances in physical chemistry, in a paper on the "Hypothesis of Radiant Matter,"[5] Loeb enumerated the objections which might be urged against the views which then obtained respecting radioactive processes.

In 1909 he assumed the duties of Chairman of our Section. The task of maintaining the high standard of the meetings set by his predecessor was no mean one, for Backeland, with his customary enthusiasm, had raised the New York Section to its greatest efficiency. Loeb devoted himself to the welfare of the Section with unremitting energy. I am keenly appreciative of what he did for the Section, as it fell to my lot to take up the task where he left it. The opportunities of the office were increased, for he had enlarged the responsibilities, as was well shown in his inaugural address that year.[1]

He did publish (1910) a paper on the "Analysis of Some Bolivian Bronzes" (with S. R. Morey),[2] and he wanted to gratify his great love for research and he did have work in progress in his private laboratory; but, in his characteristic fashion, he sacrificed personal desires to do those things he could do and others could not or were disinclined to do. We are assembled in one of the monumental evidences of this immolition.[3] He made possible the new Wolcott Gibbs Laboratory for Physical Chemistry at Harvard. In the *Proceedings of the American Chemical Society* for 1910[4] he published a beautiful obituary of Gibbs, affectionately respectful, rich in reminiscence and earnest in diction. In this hall we have an evidence of his affection for the master. Loeb visited the South American countries in behalf of the recent International Congress of Applied Chemistry. He worked long and hard on important committees in connection with the Congress. These were some of the "*other things*" he found to do for Chemistry.

The shock of Morris Loeb's death still oppresses us; but I am convinced that as time passes, and as we reach a juster evaluation of events, we shall become more and more sensitive of what this man's life really meant, and learn from it what our profession really means. He sought no office; he sought only opportunities to serve his fellowmen. He did it all with a sweet dignity that spells humility. For

"Not in hewn stones, nor in well fashioned beams,
Not in the noblest of all the builder's dreams;
But in the courageous man of purpose great,
There is the fortress, there is the living state."

CHARLES BASKERVILLE.

RESOLUTIONS PASSED BY THE VARIOUS CHEMICAL SOCIETIES ON THE DEATH OF MORRIS LOEB.

THE CHEMISTS' CLUB OF NEW YORK CITY.

WHEREAS Morris Loeb, the President of the Club, has been taken from us by death, and

WHEREAS he was the leading spirit in bringing to fulfilment ambitions and plans that had long been ours, and

WHEREAS he was always ready to shoulder burdens and to give help, and

WHEREAS he was a man of order, and of integrity in mind and in heart, sincere in scholarship, living without malice or scorn, speaking no evil, and generous in judgment, and

WHEREAS we were drawn to him by ties of deep and abiding affection, now therefore, be it

Resolved, that we make this minute of our poignant grief at his passing, and that we cherish his memory as another of his great gifts to science and to humanity.

ELLWOOD HENDRICK,
CLIFFORD RICHARDSON,
WALTER E. ROWLEY.

THE AMERICAN CHEMICAL SOCIETY.

WHEREAS Morris Loeb was a member of the New York Section of the American Chemical Society for twenty-one years, serving it in every official capacity from time to time; and

WHEREAS Morris Loeb gave generously of his sympathy to all, being especially helpful and stimulative to the younger members, while remaining a cheerful companion to those of his own age; and

[1] "The Use of the Gooch Crucible as a Silver Voltameter," *J. Am. Chem. Soc.*, **12**, 300.

[2] *Ibid.*, **13**, 263.

[3] "Is Chemical Action Affected by Magnetism?" *Am. Chem. J.*, **13**, 145–53.

[4] *J. Am. Chem. Soc.*, **27**, 1019

[5] *Pop. Sci. Monthly*, **73**, 62–60.

[1] *Sci.*, **30**, 664.

[2] *J. Am. Chem. Soc.*, **32**, 652. During 1909–10, Dr. Loeb abstracted the Italian journals for *Chemical Abstracts*.

[3] See Loeb's address at the opening of the Chemists' Club, in *Met. Chem. Eng.*, **9**, 177 (1911).

[4] Pp. 69–75.

WHEREAS Morris Loeb labored in and out of season to make the Section a power for well being in behalf of the City; and

WHEREAS Morris Loeb in his devotion to the Section labored ever faithfully for the welfare of the American Chemical Society, taking constant pride in promoting the dignity and prestige of America in the science of chemistry; and

WHEREAS the unselfish service of such a man creates a responsiveness that is real affection;

Be it Resolved, that the New York Section of the American Chemical Society record its profound appreciation of Morris Loeb as a scholarly man of science, as a loyal ever unselfish member of the Section with wide human interests. In his loss we have deep grief; in remembering him, we shall do so with affection.

LEO H. BAEKELAND,
CHARLES BASKERVILLE,
MAXIMILIAN TOCH.

THE SOCIETY OF CHEMICAL INDUSTRY.

WHEREAS the members of this Society have learned with deep sorrow of the death of their fellow member, Morris Loeb, and

WHEREAS they wish to express their high appreciation of his noble and beneficent life,

Now, therefore, be it *Resolved* that the following Minute be spread upon the records of this meeting, that a copy be sent to the Society's Journal for publication, and that a copy be suitably engrossed and forwarded to Mrs. Loeb.

Minute: Morris Loeb, chemist, investigator, educator, upright and useful citizen, altruist, philanthropist, generous patron and benefactor of arts, of sciences and of all good works, ever ready to bear more than his share of the burdens of the community and always to be found on the side of righteousness, justice and truth, lived his life of quiet power without arrogance or display, always modest concerning his own distinguished career and many accomplishments, with charity towards all and unkind criticism of none, a courteous, considerate, genial and polished gentleman of high ideals, whose chief aim and purpose was to be of assistance to his fellow man and who realized to the full that the highest reward of service is the privilege of having been of service.

Now that the temporary scaffolding of life has fallen away, the true nobility of his character stands clearly revealed in all its commanding beauty and dignity, an imperishable monument of a life's work well done and a worthy inspiration to others. Such manhood is the real glory of any country. The world is the better for his having lived in it, and we are the better for having known him.

MARSTON T. BOGERT,
CHARLES F. CHANDLER,
WILLIAM H. NICHOLS.

CURRENT INDUSTRIAL NEWS

By W. A. HAMOR.

PLUMBISM IN NEW YORK CITY.

The statement has been made that, compared with foreign countries, there has been and is very little lead poisoning in the United States. The Illinois factory commission, during the years 1908, 1909 and 1910, found 578 cases of lead poisoning in that state alone and last fall a hasty study of lead poisoning in New York City revealed 376 cases which had occurred during 1909, 1910, and 1911. These figures, including as they do only the more serious cases, become somewhat startling when we consider that in England during 1910 there were only 505 cases. Pratt (*Am. Labor Leg. Rev.*, **2**, 273) states that the cases of lead poisoning in New York City during the past three years were distributed among the following industries: white lead, lead acetate, lead oxide, dry colors, use of lead as a hardening agent, scaling paint on battleships, ship-calking, diamond polishing, printing, carpentering, plumbing, tin-smithing and painting. He made a careful study of the cases of the "leaded" ones, and found practically all the various forms of lead poisoning, ranging from light attacks of colic through wrist-drop and paralysis to death. About half of the men were comparatively young and all had received low wages. "In the white lead industry not a single man was earning over $14.00 per week, and many of them were earning less than $10.00." Out of 109 cases, 62 ate in the same room where they worked; twenty-two never washed before eating and forty-five washed only in cold water; seventy-three, or almost three-fourths, were never given oral instructions of any kind as to the dangers of their work or as to methods of preventing lead poisoning; seventy-six men never saw any posted instructions where they worked.

It is usually admitted that men addicted to alcohol are more liable to contract lead poisoning, as they are to succumb to most other diseases. But only six of the one hundred and nine men were found to use alcohol to excess; sixty-five were moderate drinkers; and thirty-one were teetotalers.

Pratt found that painting, especially interior decorating, yielded more lead poisoning than any other industry, not proportionately, but in the total number of victims. He considers that the builder should safeguard his painters by using zinc-white. With regard to plumbism in general, he concludes as follows:

"In preventing industrial disease, especially lead poisoning, an educational campaign is, it seems to me, the thing of prime importance—education of the worker and education of the employer. The first step in the education of the employee is a knowledge of the rudiments of English, then the simple rules for the care of health and self which are so effective in preventing lead poisoning. The employer, on the other hand, should be told that there is such a thing as lead poisoning, and then how to prevent it and how to treat it. There are many employers who are willing and anxious to safeguard their workers. One white-lead manufacturer is spending $20,000 on prevention."

Rambousek (*Chem. Ztg.*, **36**, 882), in a recent report on the hygiene of the German lead-color industry, considers that the most essential problem is the education of the worker to a higher standard of cleanliness. The principal technical precaution is the avoidance of dust, and personal precautions include medical examination, the supply of prescribed food and medicines, the non-use of alcohol, and the use of respirators and special wearing apparel.

The attempts at the control of plumbism date from 1876. The problem has not yet been solved.

THE CHEMICAL INDUSTRIES OF FRANCE IN 1911.

The following report on the French chemical industries is taken from *The Chemical Trade Journal*, **51**, 141:

The exports of artificial silk from France continue to grow year by year, the figure for 1911 being 179,200 kilograms as compared with 161,700 kilograms for 1910. The consumption of this product is constantly increasing, and the French firms engaged in its manufacture are unable to meet the demand, especially from Germany, where the weaving industry has taken a great development of late. A process has been invented by a Lyons chemist for manufacturing net and gauze net of cellulose, and works have been erected at St. Quentin for the

purpose of working this process, which is said to produce net closely resembling woven fabric at ¹/₄ of its cost.

The chief electrochemical products of France are calcium carbide, carborundum, chlorates, phosphorus, sodium, and explosives. The Nitrogene Co., with works at Briancon, is still experimenting with the manufacture of nitric acid by the Pauling electrical process (direct oxidation of nitrogen with the aid of electrical discharges).

The demand for chemical products in general was active and prices were satisfactory during the year, though there is nothing in particular to note. Sulphuric acid was largely consumed and heavy quantities were imported, principally from Belgium. Nitric and hydrochloric acids were not in such brisk demand. There is an increased consumption of superphosphates in manures. The law prohibiting the use of white lead for outdoor painting purposes, which comes into operation three years hence, does not appear to be in favor with the public and it is doubtful if it will come into force.

The production of beetroot alcohol from October, 1910, to September, 1911, was only 23,684,210 gallons, against 26,733,256 gallons in 1909–10. This is not surprising, as the late rainy season of 1910 prevented the sugar factories from starting as early as usual and considerably reduced the crop and value of the roots. Consequently, in spite of the stock of 6,172,100 gallons of alcohol on the Paris market at the end of September, the prices, sustained by speculation and by the small production from fruit and wines, ruled high. The production of alcohol from molasses amounted to 11,242,308 gallons for the 1910–11 season. It is predicted that the production for the 1911–12 season will be less. The consumption of denatured alcohol continues to increase throughout the republic.

THE DENATURATION OF ALCOHOL WITH PYRIDINE.

German methylated spirit contains 2 per cent. of wood-naphtha and 0.5 per cent. of pyridine bases, with, optionally, 0.125 per cent. of lavender or rosemary oil. This specification was established in 1888 by an appointed commission. While wood-naphtha contains acetone and bodies which absorb bromine, it has been generally recognized that it alone does not satisfy all the requirements of an effective denaturant. Kraemer (*Z. Spiritusind.*, **35**, 417) states that the commission, in recommending pyridine bases as a subsidiary component of the denaturing mixture, considered the following properties: Pyridine bases impart a very nauseating taste to the spirit; it may be procured easily; it is miscible with water in all proportions; it is absorbed by wood charcoal but to a limited extent at the dilution used; it is fixed by mineral acids only when these are employed in large excess; it increases the solvent properties of the alcohol; it is combustible without leaving a residuum; and it is non-toxic in the dilutions used.

None of the many substances since proposed for the same purpose has all the above desirable properties found in the case of the pyridine bases, which have continued to be used and are now obtained, not only from bone-tar as formerly, but from coal-tar oils. Kraemer looks upon the property of complete miscibility with water as one of the most important qualifications of a denaturant, and does not approve of the raising of the specification for boiling point to 160° C., whereby constituents are included which are insoluble in water and which are more easily eliminated by means of wood charcoal than pyridine.

THE STATUS OF THE ARTIFICIAL SILK INDUSTRY.

There was a marked development in the productive capacity of the artificial silk industry during the past year, particularly in Russia. The consumption is steadily increasing, and velvet manufacturers are beginning to make use of artificial silk in rather large quantities. The report just issued by the *Soie Artificielle*, the French company working the cupro-ammonium process of the *Vereinigte Glanzstoff-Fabriken, Elberfeld*, discloses a net profit of 574,365 francs, against 416,634 francs last year. The agreement with the *Soie Artificielle d'Yzieux* and the various French companies working the viscose artificial silk process is giving satisfactory results. The gross results of the Yzieux company have advanced from 511,834 francs in 1910 to 712,341 francs in 1911, and the net profits last year amounted to 423,740 francs (*Paper*, **9**, 29). The competitive ability of the guncotton artificial silk process as against the cupro-ammonium and viscose processes does not appear to improve. The Plauen Artificial Silks Works, formed in 1910, has decided to close its plant temporarily, the present high prices of alcohol in Germany making profitable working out of the question. Several plants are still operating in Belgium and Great Britain, for in these countries alcohol can still be obtained sufficiently cheap.

ANOTHER RUBBER SUBSTITUTE.

It is reported that a large factory for the manufacture of rubber substitute is in the course of erection at Ymuiden, to be in charge of an Austrian expert, Adler. The process to be put in operation is the invention of Van der Heyden, and it has been patented in Austria and Belgium.

The process of Van der Heyden is said to consist in mixing fish with 15–16 per cent. of natural rubber, producing a material which is claimed to be as elastic and strong as real rubber, but considerably cheaper; in fact, the product is said to cost about eight times less than caoutchouc. An additional advantage of the material is its reported greater resistance to heat, benzine, etc.; moreover, its vulcanization may be effected more easily and rapidly. Van der Heyden claims also to produce albumin as a by-product from the fish-flesh, and the new company has in mind the manufacture of fertilizers as well.

THE STATE OF THE PLATINUM MARKET.

Toward the end of August the platinum market was rather quiet, as consumers hoped for materially lower prices. Shortly afterwards there was further talk of lower prices, but they did not materialize, and dealers still asked $45.50 per ounce for refined platinum and $48.00 per ounce for hard metal. It was reported from Russia that sales of platinum continued small in comparison with those in the same season of the previous year, but the tendency of the large producers was not to lower the prices. It was reported from France that there were large stocks of platinum held by the Compagnie Industrielle du Platine, which controls 85 per cent. of the Russian output. However, it was said that small lots of platinum could be obtained in Ekaterinburg at a low price. The metal was quoted, on August 15, 1912, in St. Petersburg at 37,500 rubles per pood and at Ekaterinburg at 9.80 rubles per zolatnik, both for crude metal, 83 per cent. platinum.

The placers in the Urals are becoming exhausted and it is necessary to exploit the poorer placers or platinum lying lower in the stratum. The high prices of platinum in recent years, together with the question of a state platinum monopoly, has stimulated the exploitation of all the existing sources of this metal. It has been shown that neither in the Goroblagodat nor in the Nizhni-Tagil platinum region is it possible to expect a discovery of rich new placers; it is predicted that this hope can be entertained only in the north of the Urals, hitherto poorly investigated, particularly on the River Ioutyn, where outcrops of olivine rocks are shown. The Tura River for 50 miles below the mouth of the Iss is a promising dredging field, containing an immense amount of alluvial platinum, but existing laws are an effectual bar to the development of dredging on this river.

The search for platinum substitutes continues. It has recently been proposed to use tantalum instead of platinum for certain purposes, as balance weights, etc.; and earlier in the year it

was announced that a process was being exploited by the Paparoa Iron Ore Co., of Taranaki, New Zealand, for the extraction of a "hitherto unknown white metal, having similar properties to platinum" from a certain type of iron-sand found in large quantities about Taranaki. Inquiries addressed to this firm failed to bring forth any response.

INCREASING THE RESISTANCE OF ALLOYS TO CHEMICAL ACTION.

Barth (*Metallurgie*, **9**, 261) states that of the alloys of cobalt and tin, those containing but small amounts of one or other of the metals are more readily attacked by acids than the pure metals. An alloy containing 40 per cent. cobalt and 60 per cent. tin is said to be highly resistant to acids, but to be brittle and unworkable. Barth found that when this alloy is fused with four times its weight of copper, a yellow, malleable metal is obtained which is resistant to the action of dilute nitric acid. He also found that the addition of 2 per cent. of cerium to aluminum greatly increased the malleability of the aluminum, increased the solubility in dilute nitric acid, but did not affect the solubility in alkalies or hydrochloric acid.

THE PURIFICATION OF BOILER-FEED WATER.

It has been pointed out by Cribb and Arnaud (*Analyst*, **30**, 225), as the result of studies on the action of slightly alkaline waters on iron, that water containing more than a certain proportion of alkali does not rust iron. In the case of artificially softened waters, these investigators found that with small amounts of alkali, however, the action was equal in intensity to that of the unsoftened water. These results induced the view of Archbutt that it is possible after all that carbon dioxide is the chief corrosive agent, the action of which ceases when a sufficient excess of alkali has been added. Heyn and Bauer (*Mitt. Königl. Materialprüfungsamt*, **26**, 1) showed that the presence of a considerable amount of sodium carbonate in water retards the rusting of iron, although alkali carbonates are not always protective. Basch (*Chem. Ztg.*, **36**, 769) now points out that the conditions which obtain in boilers are much more complex than those under which the above experiments were made. Sodium chloride prevents the protective influence of sodium carbonate on iron, and water which has been treated with "permutite" (see THIS JOURNAL, **4**, No. 4) has a tendency to froth in the boiler, owing to the presence of alkali, and in addition causes corrosion. Basch states that while boiler-feed water is softened, it can not be said to be purified by treatment with "permutite" as the salts which produce incrustation are merely replaced by sodium carbonate and sulphate. Upon evaporation, the water becomes rich in these soluble salts and must be removed periodically. In this way, much heat is lost and the cost of treatment is increased.

THE ALKALI INDUSTRY IN GREAT BRITAIN DURING 1911.

According to the *Forty-eighth Annual Report on Alkali, etc., Works by the Chief Inspector* (*Proceedings during the year 1911*, etc.; *J. Soc. Chem. Ind.*, **31**, 715), recently issued, the number of works registered in the United Kingdom was 1463, including 167 works in Scotland; of these, 82 are "alkali" works, 8 being in Scotland. It is reported that there is again a reduction in the acidity of gases of "all chimneys," this acidity being equivalent to 1.192 grains of sulphuric anhydride per cubic foot. Operations continued active throughout 1911 in the alkali and wet process copper works. A new form of furnace, for the calcination of burned cuprous pyrites with sodium chloride, was put into operation during the year (see Ramen and Baskow, *J. Soc. Chem. Ind.*, **29**, 1459), and another form of mechanical furnace has been under trial. In fact, there has been an extended adaptation of mechanical appliances to various chemical processes. At one alkali works in Cheshire, hoods have been erected for drawing off the vapors at the time of drawing the hot saltcake from the furnaces, and it is suggested that the idea, which has proved quite successful, might be applied elsewhere with advantage; much fume may also be avoided in this operation by immediately covering the hot material with a little cold saltcake.

The year was a very active one in the cement industry. The development of the later forms of kiln still continues, while the earlier forms are steadily going out of use; this has been accompanied by a diminution in the proportion of fume given off during working, a lessening in the formation of black smoke, and the discharge of fuel gases, etc., into the air from a smaller number of higher chimneys. Rotary kilns have attained a great size and output capacity; of the six erected and started during 1911, all exceeded 150 feet in length, the longest being 230 feet.

Further progress has been made in considerably reducing the proportion of dust and fume present in the gases from smelting works, and in preventing the escape of an undue proportion of acid gases. In three works calcining zinc blende, the sulphurous gases evolved are successfully utilized in the manufacture of sulphuric acid. There was an active and general demand for sulphuric acid during the year, and consequently the works of this class were kept busy. In some cases, excessive escapes of acid gases were due to difficulties associated with working the chamber process during the unusual heat of the summer. Extended adoption of the "intensive" system of working the chamber process occurred during the year; one process in which the manufacture is carried on in towers only, that of Opl as practised at Hruschau for about three years, was put into operation toward the end of the year, with apparently successful results, a large saving in the area of ground required for a given production of acid and in the first cost of construction being effected by its adoption. Mechanical burners for pyrites, spent oxide, etc., were also more extensively introduced. In South Wales and Monmouth, new types of packing are being largely used in both Glover and Gay-Lussac towers, and in several districts a further increase in the use of fans to secure steady draught of chamber gases is reported. The steam jet blower originally used in the Kessler concentrating plant is being displaced by mechanical blowers, and the employment of silica vessels, where concentration is effected in plant of the "cascade" type, has considerably extended; "tantiron" basins have also been found satisfactory.

Mechanical devices for the removal of manufactured superphosphate from the "den," and for the simultaneous rapid removal of excessive moisture, are being more widely adopted; of late the acid effluent leaving the wash-towers has been utilized in some cases for the preparation of an alkali silicofluoride, which has a ready sale.

The relative proportion of ammonium sulphate from gas works, as compared with the total production of gas, is becoming less, owing partly to the greatly increased production of gas per ton of coal carbonized, arising from changes in methods of gas manufacture, and partly to the rapid growth of processes for the recovery of by-products from coke-oven gases and from producer gas. The "direct" method of ammonia recovery (see *J. Soc. Chem. Ind.*, **30**, 890) was brought into further use, although not to the extent which might have been anticipated. At one works in which the process has been applied successfully, a reduction of 75 per cent. in the effluent was reported. Attention has been directed to methods by which the ammonia present in crude gas may be recovered without the provision of sulphuric acid, hydrogen sulphide from the gas being utilized instead, and the Burkheiser process of producing ammonium sulphate in this manner (see *J. Soc. Chem. Ind.*, **28**, 359) is being experimented with at one works. In view of the somewhat rapid deterioration of the brick depositing chamber in the Claus sulphur recovering

process, especially at the kiln end, a sheet lead chamber has been introduced at one works, and has been found a marked improvement. As regards the waste gases resulting from the distillation of ammoniacal liquors, experience continues to show that when using oxide of iron purifiers, the heap form is to be preferred, and that the low broad-based heap has advantages over the high conical heap with comparatively restricted base.

A further installation for the manufacture of bleaching powder in a mechanically wrought plant was put into operation during the year, and is favorably noticed as minimizing nuisance from dust, escape of chlorine, etc. In view of the present over-production of the carbide industry, the attention of manufacturers is drawn to a possible new outlet for chlorine in the preparation of a series of compounds starting from the parent substance acetylene tetrachloride. (In the United States manufacturers are making inquiries concerning a commercial process for making hydrochloric acid from chlorine and hydrogen; and the possible commercial production of chlorine substitution products of methane occurring in natural gas is under investigation.) It is reported that the employment of coke towers in the production of chlorine for bleach manufacture is being given up in certain English districts, as they lead to reactions taking place which are detrimental to the formation of high-class bleach.

SULPHUR DIOXIDE FROM IRON PYRITES.

A Mechanicsville, N. Y., paper concern, which uses large quantities of sulphur dioxide in its sulphite plant in the manufacture of sulphite fiber, is contemplating the erection of a plant for the production of sulphur dioxide from iron pyrites. The ore is to be obtained from Pyrites, Canada, and will be transported to Mechanicsville by barges; after treatment, the iron ore will be sold to iron furnaces. The obtainment of sulphur dioxide by the proposed plan is new in New York, but has been in use in Virginia for several years. It is reported that sulphur dioxide can be produced from pyrites for use in paper mills at a much less cost than it can be obtained by burning native sulphur.

A HYDROGEN-SUPPLY FOR DIRIGIBLE BALLOONS.

The "Elektron" works of the *Chemische Fabrik Griesheim* have laid a line of hydrogen supply pipes from their works to the airship-harbor at Frankfort-on-Main. This line has a length of $2^3/_4$ miles and is laid much in the same way as gas pipes. Most of the joints are, however, welded, in order to avoid risks of escape of the gas, and sleeve couplings are used in only a few places. The hydrogen is obtained as a by-product in the electrolytic production of sodium hydroxide and chlorine. At the present time about 1,000 cubic meters of hydrogen can be supplied daily under a head of 1,000 mm. of water. A hydrogen gas-holder of 6,000 cubic meters capacity has been constructed near the hangar, with which it is connected by several distributing pipe lines.

"DUROBAX" GLASS.

The Jena glass works have introduced several special glasses for water-gauges. In 1891, this firm marketed "robax" glass; in 1900, "durax" glass; and quite recently "durobax" glass (*Eng.*, 94, 330). Nearly all glasses for water-gauges can stand a pressure of 200–300 atmospheres in the cold. Exposed to the action of superheated steam, all glasses will likewise fail at pressures of about 35–40 atmospheres, as the tensile strength of glass falls off very much at about 250° C. This may be determined in the Schott and Herschkowitsch apparatus, which also serves for the determination of the pressure at which a glass under high pressure and temperature will fail when suddenly played upon by a jet of cold water. This apparatus consists of a strong iron pipe, bent to a loop, and provided with sockets and glands for fixing a water-gauge at the ends; the pipe is further fitted with a pressure-gauge, a valve, and a cock for filling it with water. The whole apparatus is placed in a box and heated by a Fletcher burner. In front of the box is a small glass tube, through which cold water is kept flowing; this jet of water can, by turning the tube, be so directed that it strikes upon the water-gauge. This cold jet is repeated at pressure intervals of 2 atmospheres until the gauge cracks. Ordinary gauge glass will, under this treatment, stand only 6–7 atmospheres; "robax" glass will stand 15 atmospheres; "durax" glass, 27 atmospheres; while "durobax" glass breaks only at a pressure of 31 atmospheres. Thus the limit of resistance would in this respect almost be reached, for at a pressure of 40 atmospheres the glass would fail simply owing to thermal stress. The resistance to water-softening agents was deduced from the loss in weight which the glass showed when kept for 24 hours in steam at 8 atmospheres (171° C.) in solutions of sodium carbonate and sodium hydroxide (0.5 per cent.). "Durobax" glass lost 1.5 and 3.09 mg. per sq. cm. The loss in good feed water was 1 mg. in 31 days.

"TRIPLEX" GLASS.

"Triplex" glass, a French product, is said to be a perfectly transparent sheet or plate, which, when broken, does not fly into pieces, and which may be cracked but not smashed to bits. It is made as follows (*La Nature*, August 17, 1912): Two sheets of glass are taken and one face of each is covered with a thin layer of gelatin; the sheets, gelatin faces opposite, are placed together, with a very thin sheet of celluloid interposed. The whole is then subjected to hydraulic pressure to render the combination solid. Ordinary sheets of glass are shattered to fragments by a mass of two pounds falling 10–12 feet. "Triplex" glass is cracked, but it resists the shock and the pieces are not separated; the energy of the ball is absorbed in a much greater number of fractures, but the pieces remain adherent because of the layers of gelatin between them. Such glass may be of great service in carriages, automobiles, public conveyances, etc., and the invention should be of considerable interest to accident insurance companies.

IMPORTS AND EXPORTS OF CHEMICALS.

The imports and exports of chemicals and fertilizers, including raw materials for chemical manufactures, in the United States for the seven months ended July 31, 1912, follow. Exports include re-exports of foreign materials.

	Imports.	Exports.
Copper sulphate in pounds	....	5,504,879
Bleach in pounds	41,520,981	400
Potash salts in pounds	374,784,300	1,710,625
Soda salts in pounds	7,187,205	300,808
Acetate of lime in pounds	....	45,777,383
Phosphates in tons	....	702,767
Sulphur in tons	15,377	24,944
Pyrites in tons	555,059	....
Magnesite in pounds	128,756,843	1,333,024
Ammonium sulphate in pounds	56,560,924	357,600
Arsenic in pounds	2,983,425	850

ACID-RESISTING ALLOYS.

It is reported that Borchers has produced alloys of iron which will resist entirely the action of acids, while the articles produced can be manipulated by the usual workshop methods. The new alloys are prepared by adding from 2 to 5 per cent. of molybdenum to an alloy of ferrochrome, which contains no carbon or very little, and not less than 10 per cent. of chromium. An alloy which contained only 36 per cent. of iron, against 60 per cent. of chromium, was found to be insoluble even in boiling nitric acid, while it possessed all the usual qualities of iron and could be worked in the usual way. Not quite such favorable results were obtained by adding titanium and vanadium.

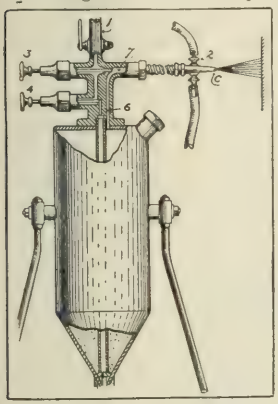
It is claimed in *Metal Industry*, Aug. 12, 1912, that if bismuth

2 parts, copper 5 parts, silicon 1 part, be melted and added to 92 parts of melted aluminum, this alloy will resist acid.

THE SCHOOP METALLIZING PROCESS.

Gradenwitz (*Sci. Am.*, **107**, 224) states that although the Schoop metallizing process was announced sometime ago, yet the details of the process and apparatus have just been made public. According to Gradenwitz, in the first metallizer constructed by Schoop, molten metal was pulverized by a jet of high pressure steam, and projected in a stream of spray upon the object to be coated with metal. This, however, required a stationary apparatus. In the portable apparatus, the molten metal is replaced by a metal powder, which is carried along by a jet of steam or of compressed gas. The jet of gas is heated either by means of a flame or an electric resistance or arc. The particles of metal powder are shot out of the apparatus by means of a jet. The object to be coated with the metal is thus bombarded with fine metallic particles. At the moment they strike the surface there occurs a transformation of live energy into heat, and this heat contributes to liquefying the particles so as to solder them to one another.

A very convenient form of portable apparatus is represented in the diagram. The mouth-piece *C*, from which the jet heated by a gas flame is blown forth, is fixed at the end of a flexible tube. The gas enters through the valve 2, into an inner tube fitting concentrically with the passage 7. The air, which is generally at a pressure of five atmospheres, passes through the tube 1, into a chamber fitted with two valves, 3, and 4. By turning the valve 3 compressed air is admitted directly into the passage 7, and by operating the valve 4 it is led into the lower half of the apparatus, where it produces a whirl of metal powder, carrying along some of the powder into the conduit 6, then into the conduit 7, and finally into the flexible tube connected with the mouth-piece. The apparatus is mounted to turn on a horizontal axis, so that the last traces of metal may be removed by the compressed air, by tipping the apparatus on its axis.



Details of the apparatus for depositing pulverized metal.

The apparatus is started by opening the gas valve 2 and igniting the gas. The compressed air admission having been opened, the valve 3 is adjusted until a satisfactory flame is obtained. Then the valve 4 is opened so as to introduce the metal powder. In order to insure a really homogeneous layer, it is essential that no oxide film covers the particles. A striking feature of the operation is that the expansion of the gas is attended by a strong cooling which solidifies the metal rapidly, while the surface temperature remains low; in fact, with such metals it is below 60° C. It is claimed that inflammable substances, like celluloid, as well as flowers and fruits can be metallized. The thickness of the deposit may vary between a hundredth of a millimeter and several millimeters, depending upon the surface to be coated, and on the relative speed of the jet. The latter also governs the hardness and density of the metal coating. This system of metallizing has been used for forming accumulator plates; constructing resistances in the form of a metal thread of zig-zag shape; obtaining electric contacts instead of soldering them; and metallizing the clothes of electricians.

THE STATE OF THE ANTIMONY MARKET.

While 75 tons of antimony ore were produced in the United States in 1910, this was entirely used for experimental purposes; and in 1911 there was no production, notwithstanding the fact that the antimony imported in the form of ore, regulus or metal amounted to 10,975,844 pounds. This was in part to be attributed to the low price ($0.08 per pound) at which the antimony was selling, but in the main to the high requirements for ore, namely, 50–60 per cent. antimony content. There is a great possibility that the ores of Nevada and Arkansas may be utilized in the near future, for there are mines capable of furnishing the American demand and successful experiments have already been made to increase the grade of production; but the market must be strong and the prices higher than those of the past year.

In October, dealers in antimony, which is extensively used in this country—antimonial lead being largely used by manufacturers of type metals, babbitt metals, and metal novelties; the sulphide in medicine; and the oxide in the ceramic and enamel industries—quoted Cookson's brand at $0.10125 per pound, Hallett's at $0.095, and Chinese, Hungarian and other outside grades at $0.09. The demand was good, but the advance in price was ascribed to a scarcity of ore. The largest producer, China, where the condition of the antimony industry has been changing rapidly during late years, is now reported as having about exhausted its deposits; if this is found to be correct, according to a prominent firm, "we shall see a high antimony market until some country is found to take the place of China as a producer of antimony ore." While the production of Germany, Hungary, Italy, and Turkey has been considerable, the prospects for American production appear to be brighter than hitherto.

POROUS METALS.

Hannover (*Compt. rend.*, **154**, 1594) finds that when a binary alloy containing a greater percentage of the one component than corresponds with the eutectic composition is centrifugalized while in the somewhat pasty condition, the eutectic can be expelled, leaving the component in excess in a porous state. Using an alloy of lead and antimony containing 90 per cent. of lead, and one of tin and lead containing 80 per cent. of tin, Hannover obtained both porous lead and porous tin. In a similar manner, from an alloy of lead with an excess of antimony, porous antimony was obtained. It is stated that the porous lead so obtained may be employed in making accumulator plates of very large capacity. According to a Berlin correspondent (*Sci. Am. Suppl.*, **74**, 133), exhaustive tests of accumulator plates made from such porous metal, conducted at the central workshops of the Danish State Railway, have shown the new type of plate to give very great capacities. Whereas the means of increasing the surface of accumulator plates so far employed (perforating and ribbing) at the most give a surface 8 times as large as the natural surface, Hannover has been able by his process to increase the natural surface about 130 fold, the number of hollows being 20 per millimeter. Porous metals could also be used for filtering; as bearing-metal, the oil being fed through the pores; for plugs in conduits containing explosive gases; as catalyzers for chemical reactions; etc.

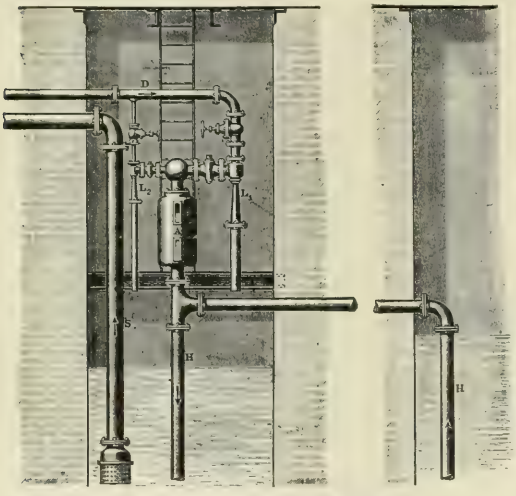
PEAT FUEL FOR THE PRODUCTION OF POWER.

Large supplies of peat are available in Portadown, Ireland, and *Engineering News*, **68**, 520, states that a plant there has run since September, 1911, on this fuel, which is fired as it comes from the drying yard. On a test producer run of 6 hours duration, with a load of 250 B. H. P., the peat consumption averaged 2.55 pounds per B. H. P. hr. with a fuel containing 18.98 per cent. of water. Two producers were running and the loads were considerably below the total capacity of the plant; this

load could, in fact, be safely carried with either producer working singly. Fuel containing as much as 70 per cent. of water has been used and the plant worked well. The separation of tar from the gas has been the chief difficulty to overcome. It has been found to be better to rely on water sprays than coke scrubbers, for the latter rapidly clogged. The main portion of the tar is thrown out into a tar sump by a centrifugal extractor, but unless the gases are subjected to a thorough washing and cooling it has been found that certain portions get past into the gas-engines. The precise amount of water necessary has been determined for the cooler to ensure condensation of the tar vapor before reaching the extractor, and thus the amount of tar in the gas at the engines is small and the valves require cleaning only once a week. At first, the plant and producers required thorough cleaning once a week, but at present they can be run for three weeks. The washing water is now 7 gallons per B. H. P. hr. The cost of running the factory on coal was about $155.00 per week, compared with $80.00 on peat, not allowing for extra labor. The peat has the following average composition: Carbon, 24.75 per cent.; volatile matter, 55.17 per cent.; water, 18.98 per cent.; and ash, 1.10 per cent. The gas resulting therefrom has a calorific value of 144 B. t. u. per cubic foot. Apparently by-product producers are not used, for no mention is made of ammonium sulphate recovery.

A NEW WATER-JET AIR-PUMP.

The water-jet air-pump illustrated herewith, of German manufacture, is intended for use in operating siphons, centrifugal pumps, pulsometers, for exhausting the air from vacuum chambers, etc.



A.—Air chamber. D.—Water supply
H.—Siphon arrangement. S.—Suction pipe of the pump.
L_1, L_2.—Water jet air-pump.

THE PARKINSON PATENT FURNACE.

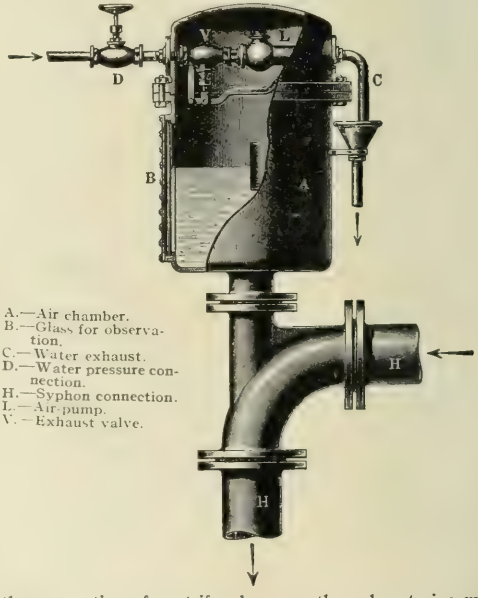
With many grades of fuel, especially those of the lignite variety where moisture, volatile matter and ash are high, it is difficult to obtain efficient combustion. The Parkinson patent furnace, described in *Power*, **36**, 367, is especially designed for use with low-grade fuels. This furnace has five distinctive features: a large ash-pit which closes air-tight; individual rocking water-cooled grates; a deep firebox accommodating a fuel bed 14–24 inches deep; a primary air system supplying air to the ash-pit under the fuel bed together with the required moisture, usually in the form of exhaust steam from the fan engine; and a secondary air system supplying preheated air over and beyond the fuel bed. The primary air is obtained from an engine-driven blower, the exhaust from the engine of which is utilized in the ash-pit. This air is introduced at a pressure just sufficient to force it through the fuel. The draft over the fuel is generally maintained at 0.1–0.13 inch water gauge. The quantity of secondary air is regulated at the stack damper and the damper in the supply pipe. This air is preheated in flowing between two firebrick arches of the furnace.

REINFORCED GALVANIZED SPIRAL PIPE.

There has been placed on the market a reinforced galvanized spiral pipe which is made from two strips of steel of different widths and with a continuous interlocking seam. Both strips of steel are rolled to shape on the edges and are interlocked and rolled down under very high pressure in a special machine which has been patented by the pipe manufacturers. The strips of steel are first cut to the required width from long sheets of steel and the ends are welded together. The steel is then placed on large spools. The strip used for the outside or reinforcing band comes from the steel mills in long lengths on reels. Both of these strips are fed into the machine at one end, rolled down interlocked in the machine, coming out at the other end in the shape of pipe. The pipe is smooth on the inside and has the reinforcing band running on the outside the entire length of the pipe; it can be made endless.

A NEW AUTOMATIC WATER-JET AIR-PUMP.

The pump illustrated in the accompanying diagram is capable of producing a vacuum of about 9 meters at a working pressure of 10 meters. The air-chamber cares for the air which is brought up by the movement of the water in the pipes. It is possible by means of observations through a transparent glass to ascertain whether the content of the air chamber is water or air.



A.—Air chamber.
B.—Glass for observation.
C.—Water exhaust.
D.—Water pressure connection.
H.—Syphon connection.
L.—Air-pump.
V.—Exhaust valve.

In the evacuation of centrifugal pumps the exhaust-pipe must be provided with an air-tight protection in order to permit of the formation of a vacuum throughout the air-pump. To operate the pump, the water is admitted first, and then the air; in order to stop it, the reverse is done. In operating the pump under a pressure of about 20 meters, the connecting-pipes must be placed a few centimeters under water.

THE USE OF GRAPHITE IN BOILERS.

An editorial contributor to *Power*, **36**, 430, remarks that there have been too many cases of the successful use of graphite for the prevention and removal of scale, and the avoidance of pitting in boilers, to leave its usefulness for this purpose longer open to debate. There may be a difference in views as to why and how it accomplishes it, but in numerous cases the feeding of graphite into a boiler has not only prevented the formation of new scale, but has removed large quantities of scale already accumulated. In some cases, however, graphite has been tried without success; this is undoubtedly due to the fact that graphite has its limitations—that it is efficient in some cases and not in others. Such failure is also attributable to the kind of graphite used and to the mode of application. The action of graphite in this case is certainly a mechanical one; the presence of graphite in scale destroys the adhesion of the particles, so that the scale either does not form or is easily broken up by the disturbances incidental to the ordinary operation of the boiler. It is essential that the right kind of graphite be employed. Graphite such as is sold to foundries for facing molds, has been used, with the result that considerable scale-forming material is deliberately introduced into the boiler, and not sufficient amorphous carbon is present to counteract its effect combined with that of the scale-forming material already present. The graphite used must be as pure as can be obtained and must have lubricating properties.

"Apexior" is a special paint, the base of which is amorphous carbon, which has lately appeared on the market. It is said to be used for coating the internal surfaces of boilers, forming a surface, the nature of which hinders the formation of hard scale, while any deposit formed adheres so lightly that it can be easily removed.

NOTES AND CORRESPONDENCE

THE THIRD INTERNATIONAL RUBBER EXHIBITION.

The Third International Rubber and Allied Trades Exhibition was held from September 23 to October 3, 1912, at the New Grand Central Palace, New York, under the patronage of the President of the United States, the Presidency of the Governor of the State of New York, and the Vice-presidency of Mr. H. C. Pearson. This exposition, for which delegates representing 21 different governments had been preparing for several months, was divided into three parts: first, rubber manufacture and manufacturing machinery, which occupied the main floor of the Palace; second, the allied lines, including reclaimed rubber, chemicals and compounding mixtures, on the mezzanine floor; and third, crude rubber, which filled the third floor.

On the main floor there were 47 exhibits by American manufacturers. The Bureau of Standards also exhibited here apparatus for studying the composition and properties of crude and manufactured rubber. Thirteen American rubber companies exhibited goods made from Cerqueira Pinto's Para rubber prepared by a "smokeless" process; "caucho" treated by the Pinto process is reported to be of better appearance and quality than that prepared previously under any other system. The makers of rubber machinery made a splendid display of their products, and some of the machines were supplied with power and could be seen at work. These exhibits are described in *The India Rubber World*, **47**, 24–31.

The Allied Trades Section included 21 exhibits by manufacturers of rubber strengtheners and preservers, regenerated rubber, deresinated products of Pontianak, lithopone, zinc oxide, mineral rubber, compounding materials, colors, and substitutes. One of the interesting features of this section was the exhibitions of stocks of reclaimed rubber by seven American reclaimers, each of whom claims distinctive features for the stocks marketed: alkali, acid, mechanical, and electrolytic processes of reclamation are in use in this country, and the advances which have been made in the industry were shown by the uniformity, cleanness, low density, high tensile strength, stretch and recovery of the stocks.

The Crude Rubber Section contained 31 exhibits. Here was the Brazilian Exhibit, the most impressive in the Exposition—one which had been planned with great care, as was shown by its comprehensiveness. It covered about 15,000 square feet and included charts, photographs, models, and specimens, relating not only to rubber but to the other great industries of Brazil as well. A pyramid of Para rubber, weighing 30 tons, surmounted by a large sphere of the same material, over 1,400 pounds in weight, was a unique feature of the exhibit. It was pointed out that the exports of Brazil in the last 20 years have increased 251 per cent., that rubber stands second to coffee only in point of importance among the Brazilian exports, and that while Brazil exported 31 tons of rubber in 1827, the exportation in 1911 was 36,547 tons. The maximum year was in 1909, when 39,026 tons were exported. It was stated that so far Brazil has had no serious competition to fear from the other rubber-producing countries. A 219 page brochure was issued by the Brazilian Government for distribution at the exhibition; this treats in a most comprehensive manner of the status of the crude rubber industry.

The exhibit of the Moro Province, Philippine Islands, showed that while rubber culture was begun only seven years ago, there are now several flourishing plantations in the Province and rubber is no longer an experiment there. Some fine pale unsmoked sheet Para was shown, as well as smoked Para in blocks. There were also smoked Ceara block and Castilloa virgin scrap. It is said that in the Moro Province, 5-year-old Para rubber trees have averaged $^3/_4$ pound per tree and that the cost per pound for producing dry rubber of the very finest quality ready for shipment has been $0.33 per pound. The rubber sold at auction in London in 1910 realized $2.63 per pound.

The rubber exhibited in the Hawaiian booths was chiefly Ceara, the first seeds of which were planted in Hawaii in 1897. The yield for 1912 will be about 6,000 pounds. The opportunity for small planters is said to be promising.

The Government of Burma, India, was represented by samples of plantation rubber from five leading estates. Samples of the balls and crepe produced from *Chavenessia esculenta*, exported as "Rangoon rubber," were also on show; the vine from which this rubber is collected by natives grows wild in the virgin jungles, often attaining a length of 300 feet. The vine gradually kills the forest trees to which it attaches itself and is consequently under a ban of extermination in the Government Teak Reserves.

The object of the exhibit of the Imperial Institute of London was to illustrate the rubber resources of the British Empire by means of specimens from the collections of the Institute. Rubber from 27 parts of the British Empire included Para from India, Ceylon, Straits Settlements, British North Borneo, Gold Coast, Nigeria, Uganda, Zanzibar and Trinidad. In 1898, rubber began to be planted as a commercial enterprise in British Malaya and there are now over 900 rubber estates; it is estimated that about 26 millions of pounds have been expended in the development of rubber plantations. Besides Para, Ceara rubber and Castilloa rubber are produced in Ceylon, although the latter two are of small importance as a source of supply; certain new species of Manihot are under trial: 215,000 acres of rubber made up the total area planted in 1911, in which year 3,194 tons were exported. It is estimated that 5,500 tons of rubber will be exported from Ceylon in 1912.

In connection with the exhibition, a conference of rubber manufacturers, producers and experts was held for the purpose of promoting knowledge of crude rubber and rubber products. A number of special papers were presented and in the topical discussions on specifications for fire hose, steam hose, insulated wire, and packings much of interest was brought out. The next International Rubber Exhibition is to be held in London in June, 1914. W. A. HAMOR.

THE UNDERWRITERS' LABORATORIES EXTRACTION APPARATUS: A NOTE.

Received September 26, 1912.

Editor of the Journal of Industrial and Engineering Chemistry:

On page 535 of your July number of this year, under the heading "The Underwriters' Laboratories Extraction Apparatus," the Chemical Department of the Underwriters' Laboratories is credited with the design of an extractor that was in reality designed by Mr. G. T. Cottle, the chemist of the New York Insulated Wire Co., some four years or more ago. The Underwriters' Laboratories are indebted for the idea to a drawing of Mr. Cottle's apparatus that was given them a little over eighteen months ago. Several months before the article in question was received by you, Mr. Cottle exhibited blueprints of the most recent form of it to various chemists of the rubber industry who had not previously been informed about it and arranged to send copies to such as were interested, and it is already known to a considerable number of analysts of rubber as the "Cottle extractor."

The author of this article further credits the Chemical Department of the Underwriters' Laboratories with having "spent several years in developing methods and apparatus to be used in a standard procedure for chemical tests of rubber compounds used on wires and cords," which methods they are ready to distribute. I therefore feel obliged to state that the methods referred to, a copy of which has since been sent me, are actually the joint work of several chemists of the insulated wire industry and that they completed the work without the smallest assistance from the Underwriters' Laboratories. The complete procedure was then given to the Underwriters' Laboratories, who, excepting one or two slight verbal changes, the result of which was to make the procedure somewhat less definite, and the addition of alternative methods for ash and total sulphur, also tending to make them less definite, published it verbatim as the "Underwriters' Laboratories' Methods of Procedure for Chemical Tests of Rubber Compounds Used on Wires and Cords." Appended to this, on a sheet marked "Extractors, Underwriters' Laboratories Inc." they publish a copy of the drawing that had been given them of the Cottle extractor.

I am informed that the author of the article in the July number of THIS JOURNAL is not connected with the Underwriters' Laboratories and does not represent them in any way. He was probably laboring under the misunderstanding that would naturally result from the manner in which this material has been published by them, a misunderstanding that seems to be somewhat wide-spread. The men who gave this procedure to the Underwriters' Laboratories presumably acted in that spirit of helpfulness that is common enough among chemists. They could hardly have anticipated the liberties that were to be taken with their work. In the case of the Cottle extractor I think some public acknowledgment is due the actual designer of the apparatus. The design is novel and presents certain practical advantages over previous extractors that become obvious under the conditions of service required by the rubber analyst. First of all it is extremely simple. It consists merely of a spiral condenser of one-eighth inch block tin tube that will slip into the neck of an ordinary 300 cc. Erlenmeyer flask of Jena glass, which forms the external part of the apparatus, and an extraction cup which hangs from the condenser, and which, in its latest form, is simply a piece of glass tube with a wire gauze bottom. Such flasks are always ready to hand, and both condenser and extraction tube can be made by the chemist in a few minutes from stock materials. It costs only a fraction of the price of an ordinary extraction apparatus to make it, and it is much less liable to breakage. It dispenses altogether with joints, which for various reasons are generally unsatisfactory, however made. As compared with the Wiley extractor, which it resembles in some respects, it has the advantage of better means for handling the extract, of greater simplicity of construction, of being more readily heated, and of not requiring any support to hold it upright. In general convenience and effectiveness it leaves nothing to be desired.

The apparatus as described in the July number of THIS JOURNAL presents no practical advantage that was not present in Mr. Cottle's original design. It does show some not very obvious changes in detail that are either immaterial or to its disadvantage. By making the flask taller and narrower the apparatus is made top-heavy. Nothing is gained in convenience by this. The chemical balances in commonest use can take a 300 cc. or even a 500 cc. flask, and those that cannot, can be provided with a suitable pair of wide bows to support the pans at a cost of fifty cents. The addition of a cap to the condenser is unessential unless the apparatus is used on a water bath, and a water bath is not a suitable means of heating an extractor of this type, even if covered. The special form of flask and the condenser with cap have the additional disadvantage of having to be made by experts, so that the chemist is made more completely dependent on the manufacture of apparatus for his parts. The same is to some extent true of the use of the Gooch crucible as an extraction cup. So altogether the result is to increase the cost without increasing the value.

For all that is effective in the design of this extractor the Underwriters' Laboratories are indebted to Mr. Cottle's drawing, as originally submitted to them, and he is entitled to full and exclusive credit for it. Under the circumstances it is a matter of surprise to me that the Underwriters' Laboratories have not already made public acknowledgment of this themselves.

Very truly yours,

G. H. SAVAGE.

18 WALNUT STREET,
WORCESTER, MASS.

BUREAU OF STANDARDS ANALYZED SAMPLES.

The Bureau of Standards, Washington, D. C., is now prepared to issue pure sodium oxalate for use as a standard in oxidimetry, in bottles containing 120 and 200 grams, the fees for which are respectively $2.00 and $3.00. With each sample is furnished a certificate giving the purity of the material, and brief directions for its use in the standardization of permanganate solutions.

Circular No. 40, on "Sodium Oxalate as a Standard in Volumetric Analysis," is now ready for distribution and will be sent upon request. It includes a description of properties, preparation and testing of sodium oxalate, and a discussion of its suitability as a standard in oxidimetry and acidimetry.

The fourth edition of Circular 25, "Standard Analyzed Samples—General Information," is now ready for distribution. Attention is called to the fact that the fee for sample No. 24, Vanadium Steel, has been changed from $2.00 to $2.50.

Chrome-tungsten Steel, No. 31, is now ready for distribution.

THE DETERMINATION OF BENZALDEHYDE, MARASCHINO CHERRIES AND MARASCHINO LIQUEUR: A CORRECTION.

In the article on this subject on page 589 of the August number of THIS JOURNAL the directions for the procedure (opposite Table IV) should read, "Add 10 cc. of the reagent," etc., instead of 100 cc. A. G. WOODMAN.

PHENOL-FORMALDEHYDE CONDENSATION PRODUCTS: A CORRECTION.

In the article on "Phenol-Formaldehyde Condensation Products," published in the October number of THIS JOURNAL, an inaccuracy has occurred.

On page 741, second column, second line, strike out "50° or" so as to make the sentence read: "This tendency to foam becomes pronounced only at temperatures above 100° C., etc."

L. H. BAEKELAND.

BOOK REVIEWS

Industrial Chemistry. A Manual for the Student and Manufacturer. By ALLEN ROGERS AND ALFRED B. AUBERT, with thirty-four collaborators. Octavo, 854 pages, 340 illustrations. New York: D. Van Nostrand Co. Price, $5.00.

The suggestion has often been made that the difficult problem of writing a book on industrial chemistry could easily be solved by having each subject treated by a specialist. This volume is made up of a series of chapters contributed by well-known chemists, engineers and manufacturers and the book will be studied with great interest by everyone familiar with the problems involved in the presentation of works on applied chemical processes. The selection of topics and the arrangement of matter is a serious editorial problem on account of the vastness of the field to be covered and the diversified interests of the readers. The specialist is interested in facts, figures and details while the teacher and student must of necessity deal with principles. The book cannot be said to meet the difficult problem of presenting, in one volume and by the same treatment of subjects, both a works managers' handbook and a students' text-book.

Another difficulty encountered in this composite book is the lack of uniformity in the scope, method of presentation and analysis of the subjects presented. Some of the chapters are very elementary, general descriptions and others are devoted almost entirely to definitions without any attempt to discuss industrial principles or practices. The main value of the work is found in the subjects which have been treated as manufacturing and industrial problems and based upon the applications of physical and chemical principles which are duly and clearly set forth.

The chapter on general processes shows the effect of too much pruning. Some of the most important fundamental processes have been omitted and others should have been elaborated and illustrated. Stamp mills, Griffin mills, cement kilns, pumps, montejus, etc., might have been described and illustrated and multiple effect evaporation, solution, extraction and drying apparatus deserve fuller treatment. This is followed by a short descriptive chapter on some of the materials used in construction.

Water for industrial purposes is well treated, but might have been accompanied by fuller descriptions and illustrations of gravity, pressure and sand filters and by cuts of open and closed feed water heaters.

The fuels chapter discusses gaseous, solid and liquid fuels, describes and illustrates two of the standard forms of pyrometer, the Mohler calorimeter for solids and liquids and the Junker for gases. Wood, peat, lignite, bituminous coal, anthracite, charcoal, coke, liquid and gaseous fuels are briefly discussed in the order given.

A chapter on producer gas is given over to general discussion with numerous illustrations of the construction and operation of various types of producers. It is to be regretted that more care and accuracy could not have been used in the presentation of the theoretical principles involved. The producer reactions may be effectively used to illustrate to the student the methods available for controlling physical conditions by a proper adjustment of chemical conditions and the author might easily have greatly enhanced the educational value of this chapter by giving less rambling descriptive matter and more facts, figures and principles.

Power and power transmission have been attempted in thirty pages. If this subject is to be discussed at all in a book on industrial chemistry, considerably more space should be given to prevailing types of engines, boilers, pumps, heaters, furnaces, drafts and innumerable other fundamental considerations.

The power plant is the heart of the factory and such superficial knowledge as might be conveyed in a short chapter in a book on industrial chemistry is of doubtful value. The whole field of electrical and mechanical engineering and the practice of engineering thermodynamics is involved in power and power transmission and unless the work can be directed by men with more than a superficial knowledge of these subjects, it had better be left in the hands of the practical man.

Sulphuric, nitric and hydrochloric acids are given in three chapters (71 pages). The consumption, properties, raw materials, approved American practice and apparatus in use are all carefully treated and illustrated and the chemistry of the processes fully elaborated. Various types of apparatus, construction of functional parts, operating methods and costs are discussed. These are excellently presented chapters and represent the most recent developments in heavy acid practice.

A chapter on commercial chemicals is devoted largely to definitions of a number of the standard products. The alkali industries briefly described in this chapter might well have been treated in considerable detail. The chemistry, past and present processes of manufacture and the engineering problems involved are all of fundamental importance and have great educational value.

The commercial importance of chlorine is recognized in a good chapter discussing the electro-chemical and strictly chemical processes for the manufacture of this element and its allied products. This is followed by a short description of some electrochemical industries such as carbon, carbides, carborundum, graphite, etc. Electrochemical processes and the principles involved might well have been treated with more thoroughness and detail both on account of their great industrial importance and their potential possibilities.

Cement, plaster, clay, pottery and glass have been treated in three chapters covering forty-four pages. The chapter on glass is especially well illustrated. The four chapters covering white lead, paints, oils and pigments are followed by a good chapter on the metallurgy of iron and steel and one on fertilizers. Illuminating gas is thoroughly and excellently treated both from the standpoint of text and illustrations. This is followed by good chapters on tar, petroleum and wood distillation industries. The chapters on oils, fats and waxes, and lubricating oils are devoted largely to definitions with practically nothing on industrial processes of manufacture.

Soaps, laundering, essential oils, varnish, sugar, starch and glucose, brewing and malting, wine-making, distilled liquors, textiles, dyestuffs, paper, explosives, leather, tanning materials, glue and casein are each given a chapter.

The book is well printed, well bound and shows the results of careful proof-reading. To get out such a work is a great undertaking and the editors are to be congratulated on the degree of success they have attained. They have invited and will no doubt receive the constructive suggestions of their fellow

chemists and engineers with a view to improving future editions. Technical libraries, chemists, engineers and teachers will find this volume a necessary addition to their works on industrial chemistry. M. C. WHITAKER.

Food and Drugs. By ERNEST J. PARRY. Volume I. The Analysis of Food and Drugs (Chemical and Microscopical); Vol. II. The Sale of Food and Drugs Acts, 1875-1907. London: Scott, Greenwood & Son, 1911. (The Van Nostrand Co., Importers.) Large Octavo, 744 and 181 pages. Prices, $7.50 and $3.00.

Volume I comprises: Tea, Coffee and Cocoa Products, 40 pages; Milk, Cheese, Butter, Lard, Suet, Olive Oil, 74 pages; Carbohydrate Foods, 74 pages; Spices, Flavoring Essences, etc., 82 pages; Alcoholic Beverages, 85 pages; Flesh Foods, 58 pages; Microscopical Analysis, 11 pages; Crude Drugs and Certain Galenicals, 74 pages; Drugs Containing Alkaloids, etc., Capable of Approximate Determination, 105 pages; The Essential Oils of the British Pharmacopoeia, 20 pages; Fatty Oils, Waxes and Soaps of the British Pharmacopoeia, 22 pages; The Chemicals of the (British) Pharmacopoeia, 68 pages.

The general plan seems to be to give under each food: definitions, a very brief sketch of the source and chemical nature, and a fairly full account of analytical methods and possible adulterants with means for their detection. The arrangement of the book and the manner of treatment (which is strictly from the point of view of the British Public Analyst) are not such as to encourage its use as a text book; the chemist who is already experienced in food analysis and familiar with the standard works on the subject will find here few new methods or helpful criticism of methods, but may gain useful suggestions as to the adulterants to be sought. The analytical data quoted from various sources and the discussion of definitions from the standpoint of British law and custom also add to the value of the book.

Volume II begins with an introduction which gives a convenient outline of the scope and content of each of the British Acts relating to foods or drugs. Then follow "The Sale of Food and Drugs Act, 1875;" "The Sale of Food and Drugs Act Amendment Act, 1879;" "The Sale of Food and Drugs Act, 1899;" "The Margarine Act, 1887;" "The Butter and Margarine Act, 1907;" a General Index and an Index of Cases.

The text of each act is given section by section with full explanation and discussion and often with illustrative cases. To those who have to do in any way with the drafting or interpretation of our food laws, the British practices and experience as recorded and explained by Mr. Parry, who is both a member of the Society of Public Analysts and a Barrister-at-Law, should be of much interest and importance.

H. C. SHERMAN.

Die Analyse der seltenen Erden und der Erdsäuren. By PROF. DR. R. J. MEYER AND DR. O. HAUSER. Stuttgart: Ferdinand Enke, 1912. 10 M.

The appearance of this book at this time is of peculiar interest, inasmuch as the importance of the chemistry of the rare elements is daily increasing, largely due to the uses made of them in the incandescent gas mantle, the incandescent electric light, the flaming arc lamp, the Nernst glower, and in the metallurgy of modern steel.

Probably no two chemists better fitted by experience with these elements could have been selected to bring together the matter herein presented than R. J. Meyer and Otto Hauser.

The literature has been thoroughly reviewed and the subject matter is well presented. In addition to the qualitative and quantitative treatment, a large amount of space is devoted to the general characteristic chemistry of the elements and also to the conventional methods of separation, which latter in many cases are not adaptable for analytical work. As a result, the book will prove of great value to those who desire to work with the rare earths—zirconium, titanium, columbium, and tantalum.

The book is a valuable contribution, containing as it does all of the important analytical methods in this field, together with the essential descriptive matter pertinent to their chemistry.

VICTOR LENHER.

Researches in Cellulose. Vol. III, 1905–1910. By C. F. CROSS AND E. J. BEVAN. pp. 170. Longmans, Green & Co. Price, $2.50, net.

The third volume of the Researches in Cellulose (1905–1910) has been developed along the same lines as the first two volumes which included the Researches of 1895–1900 and from 1900–1905. The preparation of the present book was delayed to include the research work of 1911.

The subject matter is divided into five chapters with following general headings: I. General Review; II. Cellulose; III. Cellulose Esters; IV. Ligno Celluloses; V. Technical Developments.

The authors have provided in their third volume of the Researches in Cellulose, a valuable addition which will be appreciated by all interested in the scientific or technical development of cellulose. O. KRESS.

Methods of Organic Analysis. By HENRY C. SHERMAN, PH.D., Professor of Food Chemistry in Columbia University. Second Edition, rewritten and enlarged. New York: The Macmillan Co., 1912. Price, $2.40, net.

This work, first published in 1905 by Professor Sherman for the use of his chemistry classes in Columbia University, now appears rewritten and considerably enlarged both in volume and scope. Designed primarily to cover the subjects grouped under the general title of food chemistry, it has now been enlarged to cover solid and liquid fuels, industrial alcohol, drying oils, petroleum, etc.

We consider it to be an excellent book for the use of students and for general purposes of instruction. Besides frequent foot-notes, each chapter concludes with references to the special books bearing on the subject treated and to quite a full list of journal references chronologically arranged.

While not intended to be encyclopaedic or to review all methods in use as do works like Allen's "Commercial Organic Analysis," or to convey information as to the composition of food products as does Leach's "Food Inspection and Analysis" in its tables of analyses, the purely analytical side is very fully covered. For instance, Chapter III, on Carbohydrates, General Methods; Chapter IV, on Special Methods of Sugar Analysis; and Chapter V, on Starch and Amylase, cover in a most admirable and thorough way these important related classes. Many of the special qualitative tests first described by Mulliken in his "Identification of Pure Organic Compounds" have been tested by the author and are discussed at some length.

In the chapter on fuels, the author reviews the methods of determining calorific power by the use of the different bomb calorimeters and the relations of chemical composition and calorific power of organic compounds, noting the general formulas for calculation of calorific power from the results of ultimate analyses and illustrating the subject by experimental work of his own. Much attention is given in the discussion of food analytical subjects to the methods of the Association of Official Agricultural Chemists and in several cases the proposals of the International Commissions for the Unification of the Methods of Analysis of special industries are given.

In addition to the book and journal references before referred to, as accompanying each Chapter, the book has a satisfactory subject index and is thus made a practical and convenient book for the student. It ought to meet very general acceptance from all interested in the analysis of food products and allied substances. S. S. SADTLER.

NEW PUBLICATIONS

By D. D. BERGLZHEIMER, Librarian, Chemists' Club, New York.

Acids; The Mineral— of the Chemical Industry. By G. F. JAUBERT. 8vo. Price, $4.00. Gauthier-Villars, Paris. (French.)

Analysis; Volumetric—. By CHARLES H. HAMPSHIRE. 8vo. Price, $1.00. J. & A. Churchill, London.

Analyst's Laboratory Companion. By ALFRED E. JOHNSON. 4th Ed. 8vo. Price, $1.75. J. & A. Churchill, London.

Brickmaking; Modern—. By ALFRED B. SEARLE. 8vo., 440 pp Price, $5.00. D. Van Nostrand Co., New York.

Cements and Hydraulic Limes. By L. BERTELLI. 8vo., pp. 572. Price, $2.25. Milan, 1912. (Italian.)

Chemistry; Practical—, Including Simple Volumetric Analysis and Toxicology. By P. A. ELLIS RICHARDS. 8vo., pp. 149. Price, $0.75. Balliere, Tindall & Co., London.

Chemistry; Theoretical and Physical—. By S. L. BIGELOW. 8vo., pp. 544. Price, $3.00. Century Co., New York.

Colorists; Yearbook for— Dyers, Vol. XIV for 1911. By HERMAN A. METZ. Sm. 8vo., pp. 503. Farbwerke-Hoechst Co., New York.

Copper; Modern—Smelting. By D. M. LEVY. 8vo., pp. 272. Price, $2.75. Chas. Griffin & Co., London.

Drying by Means of Air and Steam. By E. HAUSBRAND. 2nd Ed. Cr. 8vo., pp. 80. Price, $1.25. Scott, Greenwood & Co., London.

Explosives; Historical Papers on Modern—. By G. W. MACDONALD. 8vo., pp. 192. $2.50. Whittaker & Co., London.

Explosives; Notes on Military—. By ERASMUS M. WEAVER. 3d Ed. 8vo., pp. 358. Price, $3.00. John Wiley & Sons, New York.

Foods; Their Origin, Composition and Manufacture. By WILLIAM TIBBLES. 8vo., pp. 950. Price, $4.50. Ballière, Tindall & Co., London.

Foundry; Notes on— Practice. By J. J. MORGAN. 8vo., pp. 108. Price, $0.75. Charles Griffin & Co., London.

Inorganic Chemistry; A Laboratory Manual of—. By J. B. EKELEY. Cr. 8vo., pp. 128. Price, $1.25. John Wiley & Sons, New York.

Inorganic; Modern— Chemistry. By J. W. MELLOR. 8vo., pp. 871. Price, $2.20. Longmans, Green & Co., New York.

Inorganic; Recent Advances in Physical and— Chemistry. By A. W. STEWART. 8vo., pp. 272. Price, $2.50. Longmans, Green & Co., New York.

Inorganic; Treatise on— Chemistry. By E. MOLINARI AND E. FEILMANN. 8vo. Price, $5.25. J. & A. Churchill, London.

Iron; The Chemical Analysis of—. By A. A. BLAIR. 7th Ed. 8vo. Price, $4.00. J. B. Lippincott Co., Philadelphia.

Microscope; The— and its Use. By HERMANN HAGER AND CARL MEZ. 8vo., pp. 375. Price $2.50. Julius Springer, Berlin. (German.)

Mining; Index of— Engineering Literature, II. By WALTER R. CRANE. 8vo., pp. 445. Price, $3.00. John Wiley & Sons, New York.

Petroleum; The Chemistry and Physics of—. Vol. I, Part I. By C. ENGLER. 8vo. Price, $7.00. S. Hirzel, Leipzig.

Progress of Chemistry; Annual Reports on the— for 1911. Chemical Society (London). By J. C. CAIN. 8vo.. pp. 319. Price, $2.00. Gurney & Jackson, London.

Retort; Modern— Settings: Their Construction and Working. By T. BROOKE. 8vo., pp. 200. Price, $3.00. John Allan & Co., London.

Rubber; Euphoria lorifoila, a Possible Source of— and Chicle: Physical and Chemical Properties. By WM. MCGEORGE AND W. A. ANDERSON. 8vo., pp. 16. Hawaii Agricultural Experiment Station, Honolulu.

Scientific American Reference Book for 1913. By ALBERT A HOPKINS AND A. RUSSELL BOND. L. 8vo., pp. 608. Price, $1.50. Munn & Co., New York.

Silk; Raw—. By LEON DUCAN. 8vo. Price, $2.50. Silk Publishing Co., New York.

Soap Makers' Handbook. By WILLIAM T. BRANNT. 2nd Ed. 8vo., pp. 535. Price. $5.00. Henry Carey Baird & Co., Philadelphia.

Starch; A Method for the Determination of— in Meat Food Products. By T. M. PRICE. 8vo., pp. 6. U. S. Dept. of Agriculture, Bureau of Animal Industry, Circular No. 203.

Sugar; The Management of Steam in the— Factory. 2nd Ed. 8vo., pp. 175. Price, $1.50. Schallehn & Wollbrueck, Magdeburg. (German.)

Sugar; The World's Cane— Industry, Past and Present. By H. C. PRINSEN GEERLIGS. Roy. 8vo., pp. 400. Price, $3.00. Norman Rodger, Altrincham.

Textile; Mechanical and Physico Technical— Examination. By P. HEERMANN. 8vo. Price, $2.50. Julius Springer, Berlin. (German.)

Water Analysis. By HERBERT B. STOCKS. 8vo., pp. 136. Price, $1.25. Chas. Griffin & Co. London.

Water Purification and Sewage Disposal. By J. TILLMANS. L. 8vo., pp. 157. Wilhelm Knapp. Halle. (German.)

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Alcohol; The Chemical Effects of Methyl and Ethyl—. By HANS VON LIEBIG. *Archiv der Pharmazie*, Vol. 250, 1912, No. 6. pp. 402–413.

Caseins; Technical—, their Examination and Valuation. By W. HOEPFNER AND H. BURMEISTER. *Chemiker Zeitung* Vol. 36, 1912, No. 112, pp. 1053–1054.

Colors; The Aspect of— under Artificial Light. By DAVID PATTERSON. *Cotton*. Vol. 76, 1912, No. 11, pp. 464–466.

Copper; The Electrolytic— Refining Industry. By JOHN B. C. KERSKAW. *Chemical World*. Vol. 1, 1912, No. 10, pp. 343–345.

Corrosion; Passivity of Iron under Boiler Conditions. By HORACE G. BYERS AND FLOYD T. VORIS. *Journal of the American Chemical Society*, Vol. 34, 1912, No. 10, pp. 1368–1379.

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Gas; The Analysis of Water— Purification Material. By E. C. UHLIG. *Gas Institute News*, Vol. 1, 1912, No. 9, pp. 419–434.

Gas; By-products in— Manufacture. By CHARLES E. MUNROE. *Progressive Age*, Vol. 30, 1912, No. 19, pp. 822–830.

Hydrogen; Determination of— and Methane in Gas Mixtures. By WALTHER HEMPEL. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912 No. 36, pp. 1841–1845.

Manganese; Determination of— as Sulfate and by the Sodium Bismuthate Method. By WILLIAM BLUM. *Journal of the American Chemical Society*, Vol. 34, 1912, No. 10, pp 1379–1398.

Paper; The Analysis of—. By B. SETLIK. *Paper*, Vol. 9, 1912, No. 1, pp. 15–17.

Peroxid Production, Past and Present. By J. S. BREWER. *Druggists' Circular*, Vol. 56, 1912, No. 10, pp. 609–613.

Petroleum; Chemistry and Technology of— in 1911. By L. GURWITSCK. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No 37, pp. 1897–1904.

Refrigeration; The Power Required for—. By JOHN J. SMITH. *Metallurgical and Chemical Engineering*, Vol. 10, 1912, No. 10, pp. 657–659.

Rubber; The "Insoluble" Constituents of Para— and its Influence on the Quality of the Rubber. By CLAYTON BEADLE AND HENRY P. STEVENS. *India Rubber Journal*, Vol. 44, 1912, Nos. 11 and 12, pp. 14 15 and 15–16.

Silica; Present-Day Use of Fused— Ware in the Industries. By A. POHL. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 36, pp. 1845–1855.

Silver; The Solubility of— Oxid in Lead Oxid (Litharge). By ERNST J. KOHLMEYER. *Chemiker Zeitung*, Vol. 36, 1912, No. 113, pp. 1079–1082.

Starch; Observations on— Grains and the Counting Chamber, an Aid to the Quantitative Determination of the Adulteration of Vegetable Powders. By C. HARTWICK AND A. WICHMANN. *Archiv der Pharmazie*, Vol. 250, 1912, No. 6, pp. 452–471.

Steel, The Electric— Furnace in Foundry Practice. By PAUL GIROD. *Metallurgical and Chemical Engineering*, Vol. 10, 1912, No. 10, pp. 663–665.

Sucrose; Determination of— in the Raw Material of the Cane Sugar Industry. By H. C. PRINSEN GEERLIGS. *International Sugar Journal*, Vol. 14, 1912, No. 165, pp. 511–525.

Tanning; Comparative Analyses of— Materials. By W. K. ALSOP. *Journal of the American Leather Chemists' Association*, Vol. 7, 1912, No. 10, pp. 527–547.

Tar; The Electrical Separation of— from Coal Gas. By A. H. WHITE, J. H. HACKEE AND FRANK STEERE. *American Gas Light Journal*, Vol. 97, 1912, No. 14, pp. 210–211.

Tar Phenols; The Scientific and Technical Significance of the—. By F. RASCHIG. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 38, pp. 1939–1948.

Terpenes; The—. By J. B. COHEN. *Chemical World*, Vol. 1, 1912, No. 10, pp. 331–332.

Tungsten; Production of Ductile— (Production of Pure Tungsten, Melting Point, etc.). By OTTO RUFF. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 37, pp. 1889–1897.

Turbine; The Steam— in the Sugar Industry. By H. TREITEL. *International Sugar Journal*, Vol. 14, 1912, No. 165, pp. 504–511.

RECENT INVENTIONS

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

PROCESS OF PURIFYING HYDROGEN.

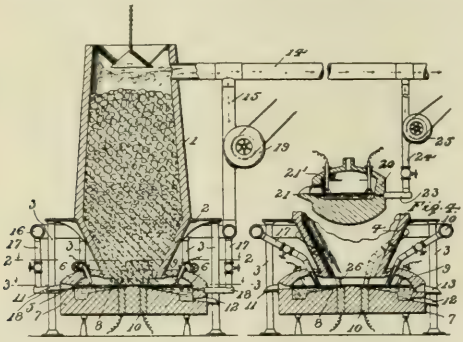
U. S. Patent No. 1,034,646, to Gustav H. Rabenalt, of Dover, New Jersey.

By this process hydrogen is freed from hydrogen sulfid by passing it into a solution of iodin in a suitable solvent and simultaneously passing an electric current through the solution. Sulfur is precipitated and the hydriodic acid formed is decomposed by the electric current into hydrogen and iodin.

METHOD OF PRODUCING REFINED METALS AND ALLOYS.

U. S. Patent No. 1,034,784, to Albert E. Green, of Pueblo, Colorado, Assignor to American Electric Smelting and Engineering Company, of St. Louis, Missouri.

In this process an ore change is smelted in a furnace of the character illustrated, and the gases from the top of the furnace are withdrawn and introduced into the bath of metal and slag



which is maintained within selected temperatures by means of an electric current passed therethrough. In this way the metal is freed from undesirable elements which are oxidized and eliminated.

PROCESS OF MANUFACTURE OF ALKALINE AND EARTHY-ALKALINE NITRATES.

U. S. Patent No. 1,036,611, to Philippe Auguste Guye and Georges Darier, of Geneva, Switzerland, and Allart van Vloten of Haarlem, Netherlands.

In order to completely convert alkaline chlorids into nitrates it is necessary to heat them several times with an excess of nitric acid. Under these circumstances *aqua regia* is formed and at the same time a large part of the excess nitric acid is decomposed

Fig. 1.

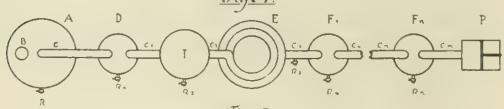
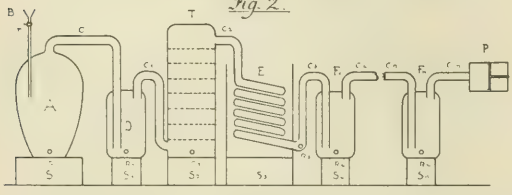


Fig. 2.



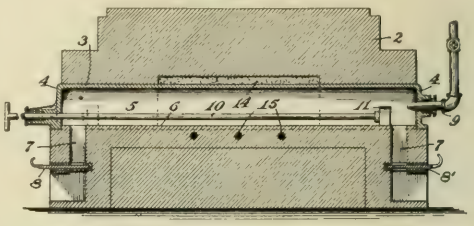
into oxides of nitrogen. The patentees avoid the disadvantages of this method by subjecting the alkali or alkaline earth chlorids to the action of nitric acid diluted to at least 35% of HNO_3 and carrying on the reaction at a temperature not exceeding 80° C. and under a pressure lower than 300 mm. of mercury.

METHOD OF PRODUCING CARBON-BLACK.

U. S. Patent No. 1,036,362, to John A. Snee, of West Elizabeth, Pennsylvania.

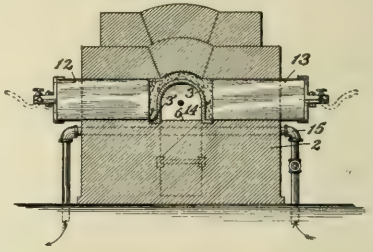
Carbon-black, if allowed to remain in the presence of the heat necessary to decompose hydrocarbon gases will coke, thereby

Fig 1.



detracting from its market value. The patentee prevents this deterioration by introducing the hydrocarbon gas horizontally into a highly heated, flame-excluded zone, the resulting carbon-

Fig 2



black being deposited upon the lower surface of the retort, this surface being maintained at a lower temperature than the zone in which the gas is decomposed.

PROCESS FOR EXTRACTING ALUMINA AND POTASH FROM FELDSPAR.

U. S. Patent No. 1,035,812, to Samuel Peacock, Assignor to American Acid Company, of Baltimore, Maryland.

The feldspar is first coarsely ground and calcined with sufficient carbonate of lime to supply at least one and not more than two chemical equivalents of CaO for each chemical equivalent of SiO_2.

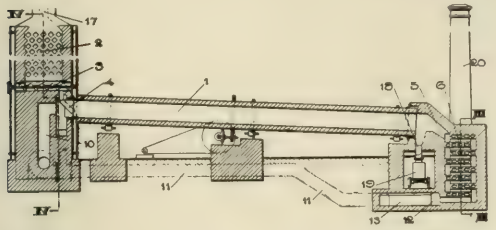
The calcined mixture is pulverized to 100 mesh and there is added sufficient soda or potash to make one chemical equivalent for each chemical equivalent of alumina present.

The mixture is boiled, preferably under pressure, and with sufficient water to make a thin paste. The alumina becomes soluble as an alkali aluminate and the silica remains insoluble as calcium silicate. The soluble and insoluble materials are separated by filtration and the aluminum recovered as alumina by passing carbon dioxid through the solution. The alumina is freed from the remaining alkali by adding one equivalent of silica for each equivalent of soda or potash present in the alumina and the mixture treated in a digester with superheated steam at a pressure of five atmospheres. When the charge is washed with water, the silica and alkali are removed as alkali silicate, leaving the alumina practically pure.

METHOD OF REDUCING IRON ORE.

U. S. Patent No. 1,033,051, to Gustaf Grondal, of Djursholm, Sweden.

This is a continuous process in the practice of which is employed an inclined cylindrical furnace mounted and kept rotating in the usual manner. One end of the furnace communicates with a device for charging the ore-carbon mixture and its other end communicates on the one hand with a discharge for the reduced product and on the other hand with a recuperator, from which the heated gas or gas mixture comes and sweeps through the furnace. The gases produced during the reduction in the furnace, consisting of carbonic oxide and carbonic acid as well as the gas or gas mixture used for heating, are led from

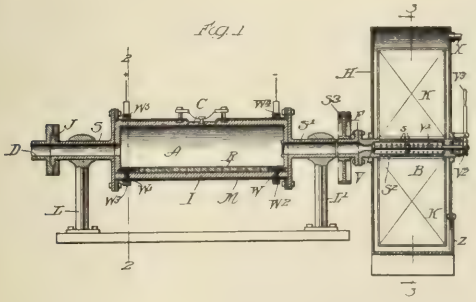


the charging end of the furnace to a fan or blower by means of which they are forced back to the recuperator and through it and after being heated to a suitable temperature, say 800° C., again through the furnace. Here they are mixed with the gases generated during the continued reduction and forced back to the recuperator and through it, and so on in a continual circulation. The excess of gases arising from the addition of the gases generated during the continuous process of reduction and which is not needed for the transmission of heat, is led away and used for heating the recuperator into which it is led and where the combustible part is burned.

PREPARING NITROGENOUS COMPOUNDS.

U. S. Patent No. 1,033,842, to Leland L. Summers, of Chicago, Illinois.

This is a process of preparing nitrogenous compounds, such as cyanogen and ammonia, together with the numerous salts derived from these compounds, the nitrogen from the atmosphere being preferably used, though other sources of nitrogen may be utilized. The process consists in treating a metallic nitride with ammonia and hydrogen in the presence of heated carbonaceous material.

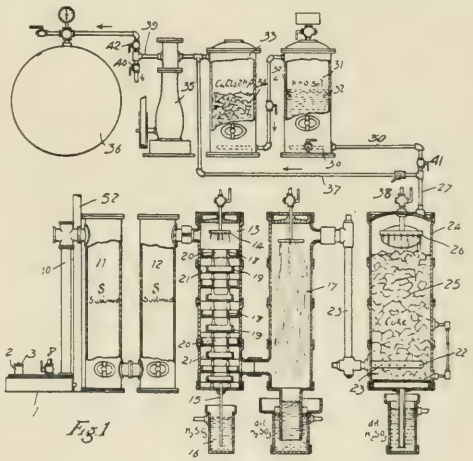


In carrying out the pocess there is placed in the drum *A* a metal which is capable of uniting with nitrogen to form a nitride, preferably an alkaline earth metal, magnesium or calcium. When metallic magnesium is placed in the retort and heated to a temperature of 400° to 500° C., and nitrogen is introduced through the shaft *S*, the retort being revolved, an intimate contact takes place between the heated magnesium and the nitrogen. If charcoal or other forms of carbon are placed in the retort in contact with the magnesium nitride, and hydrogen and ammonia introduced through the shaft *S*, the retort being revolved and a suitable current passed through the resistance *R* so that the temperature in the retort is raised to a point between 300° and 600° C., a reaction will take place in which the carbon will unite with the nitrogen of the magnesium nitride to form cyanogen; this will react with the hydrogen and ammonia, forming ammonium cyanide and hydrocyanic acid. The ammonium cyanide is readily decomposed into hydrocyanic acid and ammonium at temperatures in excess of 35° to 40° C., so that the proportions of the ammonium cyanide and of hydrocyanic acid will depend upon the amount of gases introduced and the temperatures at which they are discharged into the absorber *B*. In the absorber is placed a mixture of sodium chloride and aqueous ammonia.

PROCESS OF OBTAINING SUBSTANTIALLY PURE NITROGEN FROM THE AIR.

U. S. Patent No. 1,036,788, to Charles Blagburn, of Antioch, California.

The patentee employs sulfur to combine with the oxygen of the air. The air is directed downward upon the surface of



burning sulfur, the amount of air being so restricted that no more oxygen will be present than will combine with the sulfur.

The nitrogen, sulfurous acid and unburned sulfur are conducted away, the sulfur being deposited and the sulfurous acid washed out, leaving the nitrogen ready for use.

PROCESS OF MANUFACTURING SUBSTITUTES FOR OILS, CAOUTCHOUC, RESINS AND THE LIKE.

U. S. Patent No. 1,037,158, to Leon Lilienfeld, of Vienna, Austria-Hungary.

By heating Chinese wood oil with orthotoluidin in the presence of zinc chlorid the patentee obtains, according to the proportions of the reagents employed, a thick oil suitable for use in the manufacture of varnishes or a material which may be used as a substitute for, or an admixture to caoutchouc, guttapercha, balata or the like or a plastic mass of the nature of celluloid, horn or resin. The rubber-like product is said to be elastic, soluble in volatile solvents and suitable for many purposes for which rubber is used.

MARKET REPORT.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF OCTOBER.

ORGANIC CHEMICALS.

Acetanilid	Lb.	20 1/2	@	23
Acetone (drums)	Lb.	17	@	18
Alcohol, grain (188 proof)	Gal.	2.55	@	2.57
Alcohol, wood (95 per cent.)	Gal.	50	@	52
Alcohol, denatured (180 proof)	Gal.	40	@	42
Amyl Acetate	Gal.	2.75	@	2.95
Acetic Acid (28 per cent.)	C.	2.00	@	2.15
Aniline Oil	Lb.	10 3/4	@	11 1/2
Benzoic Acid	Lb.	23	@	27
Carbon Tetrachloride (drums)	Lb.	10 1/2	@	11
Carbon Bisulphide	Lb.	9	@	12
Chloroform	Lb.	20	@	30
Carbolic Acid (drums)	Lb.	14	@	15
Citric Acid (domestic), crystals	Lb.	38 1/2	@	39
Camphor (refined in bulk)	Lb.	44	@	—
Dextrine (imported potato)	Lb.	6	@	7
Dextrine (corn)	C.	3.00	@	—
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8 1/2	@	9 1/2
Glycerine (dynamite)	Lb.	19 1/4	@	20
Oxalic Acid	Lb.	8	@	8 3/4
Pyrogallic Acid (bulk)	Lb.	1.35	@	1.45
Salicylic Acid	Lb.	31	@	33
Starch (corn)	C.	2.25	@	2.36
Starch (potato)	Lb.	5 1/4	@	5 3/4
Tannic Acid (commercial)	Lb.	35	@	35 1/2
Tartaric Acid crystals	Lb.	30 1/4	@	31

INORGANIC CHEMICALS.

Acetate of Lime (gray)	C.	2.50	@	2.60
Acetate of Lead (brown, broken)	Lb.	7 3/4	@	8
Alum (lump)	C.	1.75	@	2.00
Ammonium Carbonate, domestic	Lb.	8	@	8 1/2
Ammonium Chloride, gray	Lb.	6 1/8	@	6 1/4
Aluminum Sulphate	C.	90	@	1.75
Aqua Ammonia (drums) 16°	Lb.	2 1/4	@	2 1/2
Arsenic, white	Lb.	5 1/2	@	6 1/8
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Barium Chloride	C.	1.40	@	1.55
Barium Nitrate	Lb.	4 3/4	@	5
Borax, crystals (bags)	Lb.	3 1/2	@	4
Boric Acid, crystals (powd.)	Lb.	7	@	7 1/2
Bromine, bulk	Lb.	25	@	30
Bleaching Powder (35 per cent.)	C.	1.35	@	1.55
Barytes (prime white, foreign)	Ton	18.50	@	22.50
Blue Vitriol	Lb.	5 1/2	@	5 3/4
Calcium Chloride	C.	65	@	90
Chalk (light precipitated)	Lb.	4	@	5
China Clay (imported)	Ton	11.50	@	18.00
Feldspar	Ton	7.00	@	9.00
Fuller's Earth, powdered	C.	80	@	85
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1.15	@	1.55
Iodine (resublimed)	Lb.	3.05	@	3.10
Lead Nitrate	Lb.	8 3/8	@	8 1/2
Lithium Carbonate	Lb.	65	@	70
Magnesite (raw)	Ton	7.50	@	8.50
Nitric Acid, 36°	Lb.	3 7/8	@	4 1/4
Phosphorus	Lb.	35	@	90
Phosphoric Acid, sp. gr. 1.75	Lb.	22	@	26
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bromide	Lb.	35	@	37
Potassium Permanganate (bulk)	Lb.	9 3/4	@	10
Potassium Cyanide (bulk) 98–99%	Lb.	19	@	24
Potassium Iodide (bulk)	Lb.	2.60	@	2.65
Potassium Chlorate, crystals	Lb.	8 1/4	@	9 1/2
Potassium Nitrate (crude)	Lb.	5	@	5 1/8
Potassium Bichromate, 50°	Lb.	6 7/8	@	7
Quicksilver, Flask		42.00	@	43.00
Salt Cake (glass-makers')	C.	55	@	65
Silver Nitrate	Oz.	40 1/2	@	41 1/2
Soapstone in bags	Ton	10.00	@	12.00
Sodium Acetate	Lb.	4 1/4	@	5
Sodium Chlorate	Lb.	8 1/4	@	9 1/2
Sodium Bicarbonate (English)	Lb.	2 3/4	@	3
Sodium Bichromate	Lb.	5 1/8	@	5 1/4
Sodium Hydroxide, 60 per cent.	C.	1.60	@	1.65
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent., spot	C.	2.55	@	—
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	6 7/8	@	7 5/8
Sulphur, Roll	C.	1.85	@	2.15
Sulphur, Flowers (sublimed)	C.	2.20	@	2.60
Sulphuric Acid, 60° B.	C.	85	@	1.00
Talc (American)	Ton	15.00	@	20.00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	13 1/4	@	13 1/2
Tin Oxide	Lb.	52	@	54
Zinc Chloride (granulated)	Lb.	4 1/4	@	4 1/2
Zinc Sulphate	Lb.	2 1/4	@	2 1/2

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	40	@	44
Black Mineral Oil, 29 gravity	Gal.	12	@	12 1/2
Castor Oil (No. 3)	Lb.	9 1/2	@	10 1/2
Ceresin (yellow)	Lb.	9	@	15
Corn Oil	C.	5.85	@	5.90
Cottonseed Oil (crude), f. o. b. mill	Gal.	36	@	37
Cylinder Oil (light, filtered)	Gal.	19 1/2	@	20
Japan Wax	Lb.	10	@	10 1/4
Lard Oil (prime winter)	Gal.	88	@	93
Linseed Oil (double-boiled)	Gal.	61	@	64
Paraffine Oil (high viscosity)	Gal.	25 1/2	@	26
Paraffine (crude 120 & 122 m. p.)	Lb.	3 1/4	@	3 3/4
Rosin Oil (first run)	Gal.	36	@	37
Spindle Oil, No. 1	Gal.	16	@	16 1/2
Sperm Oil (bleached winter), 38°	Gal.	72	@	74
Stearic Acid (double-pressed)	Lb.	9 1/2	@	10 1/4
Tallow (acidless)	Gal.	65	@	68
Tar Oil (distilled)	Gal.	30	@	31

METALS.

Aluminum (No. 1 ingots)	Lb.	25 1/2	@	26
Antimony (Hallet's)	Lb.	9 1/2	@	10 1/2
Bismuth (New York)	Lb.	2.10	@	2.15
Copper (electrolytic)	Lb.	17.45	@	17.60
Copper (lake)	Lb.	17 1/2	@	17 5/8
Lead, N. Y.	Lb.	5 1/8		—
Nickel	Lb.	50	@	55
Platinum (refined)	Oz.	46.35	@	47.00
Silver	Oz.	63 1/2	@	—
Tin	Lb.	50.05	@	50.15
Zinc	Lb.	7.55	@	—

FERTILIZER MATERIALS.

Ammonium Sulphate	C.	3.25	@	—
Fish Scrap, domestic, dried	Unit	2.50	&	—
Blood, dried	Unit	2.75	@	—
Tankage, high grade	Unit	2.60	@	2.65 & 10
Bone, 4 1/2 and 50, ground, raw	Ton	28.00	@	—
Potassium, "muriate," basis 80%	Ton	38.55	@	—
Phosphate, acid, 16 per cent.	Ton	6.75	@	7.00
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.	Ton	3.70	@	3.80
Tennessee, 68–72 per cent.	Ton	4.25	@	4 50
Pyrites, furnace size, imported	Unit	0.13 1/8	@	0.13 1/4
Castor meal	Unit	nominal		
Mowrah meal	Ton	8.50	@	9.00

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume IV | DECEMBER, 1912 | No. 12

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Contributions and communications should be addressed to the Editor, M. C. Whitaker, Columbia University, New York City.

Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly. Foreign postage seventy-five cents, Canada, Cuba and Mexico excepted.

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Penna., under the Act of March 3, 1879.

ESCHENBACH PRINTING COMPANY, EASTON, PENNA.

TABLE OF CONTENTS

EDITORIALS:
- The Research Corporation, an Experiment in Public Administration of Patent Rights ... 864

ORIGINAL PAPERS:
- A Study of the Variations of the Physical and Chemical Properties of Red Lead. By O. W. Brown and A. R. Nees ... 867
- The Continuous Purification of Coal Gas with Weak Ammonia Liquor. By J. G. O'Neill ... 876
- Studies on Fish Oils, III: Properties of Fish and Vegetable Oil Mixtures. By George F. White and Adrian Thomas ... 878
- The Relation of the Refractive Index of Soda-Barium and Soda-Lime Glasses to their Chemical Composition. By Edwin Ward Tillotson, Jr. ... 882
- Composition of the Salines of the United States, II: Natural (Subterranean) Brines and Mother Liquors from Natural Brines. By J. W. Turrentine, with analyses by A. R. Merz and R. F. Gardner ... 885
- The Determination of Zinc by Electroanalysis. By Ellwood B. Spear and Samuel S. Strahan ... 889
- The Kambara Earth. A Decolorizing Material for Mineral Oils, Etc. By K. Kobayashi ... 891
- Investigation of the Methods for the Determinations of Total Fatty Acids in Cotton-Seed Foots. By Frank N. Smalley ... 893
- The Determination of Chromium and Vanadium in Steel. By D. J. Demorest ... 895
- A Rapid Control Method for the Determination of Oil in Grains. By E. P. Harding and Lillian L. Nye ... 895
- Soy Bean Cheese. By William V. Linder ... 897

LABORATORY AND PLANT:
- A New Form of Orsat Apparatus. L. M. Dennis ... 898
- The Stormer Viscosimeter and the Value of Viscosity Determinations by its Use. By Gilbert Rigg and J. L. Carpenter ... 901
- Apparatus and Method for "Carbon Test and Ash Residue" in Petroleum Lubricating Oils. By P. H. Conradson ... 903
- A Self-Filling Measuring Wash Bottle. By O. C. Smith 905

ADDRESSES:
- A Plan for Organized Research and Analytical Chemistry in Successful Chemical Manufacturing. By William C. Ferguson ... 905
- The Electrical Precipitation of Suspended Particles by the Cottrell Processes. By Linn Bradley ... 908
- The Control of Temperature in the Operations of Analytical Chemistry. By Theodore W. Richards ... 910

CURRENT INDUSTRIAL NEWS:
- "Vitreosil" in the Nitric Acid Industry ... 913
- Development of the Sulphite Industry ... 913
- Problems in Papermaking ... 914
- The Autumn Meeting of the Institute of Metals ... 914
- Solid Oil as a Marine Fuel ... 915
- High-Pressure Gas Lighting ... 915
- The Properties of Motor Fuels ... 915
- The Consumption of Oxygen ... 915
- "Plumboxan" ... 916
- Aluminum Alloys ... 916
- Metallurgie ... 916
- A New Type of Continuous Furnace ... 916
- Artificial Silks ... 916

NOTES AND CORRESPONDENCE:
- Obituary—Thomas Price ... 917
- A Suggestion Regarding the Graduation of Hydrometers ... 917
- The Effect of "Lime-Sulphur" Spray Manufacture on the Eyesight.—A Note ... 917
- The Andrew Carnegie Research Scholarship ... 917
- American Institute of Chemical Engineers ... 918
- The Chemical Societies in New York City ... 918
- On the Starch of Glutinous Rice and its Hydrolysis by Diastase.—A Correction ... 918

BOOK REVIEWS:
- Paper Pulps from Various Forest Woods; The Metallography of Iron and Steel; Analysis of Metallurgical and Engineering Materials ... 918

NEW PUBLICATIONS ... 920

RECENT INVENTIONS ... 921

MARKET REPORT ... 922

EDITORIALS

THE RESEARCH CORPORATION, AN EXPERIMENT IN PUBLIC ADMINISTRATION OF PATENT RIGHTS.

Some seven years ago while working in the University of California on a set of problems in sulphuric acid manufacture, the author came upon certain phenomena which promised to lead to important improvements in the electrostatic collection of smoke and fumes from chemical and metallurgical plants. He was at once confronted by the old dilemma of adjustment between academic and commercial activities, as only through direct construction and study of installations on a commercial scale did it seem possible to develop into full usefulness the inventions involved.

Finally with the personal and financial help of Prof. Edmond O'Neill, of the Chemistry Department, and Dr. Harry East Miller and Mr. E. S. Heller, both alumni of this Department of the University, the commercial development of the project was undertaken and patents secured. The understanding among those thus actively concerned was that when the receipts from the business should have repaid the initial investment with reasonable interest at least, a considerable portion of the patent rights should be turned over to the University of California, or some other public institution, to be administered as the nucleus of a fund for the promotion of research; it was also hoped that this might set a precedent and stimulate similar contributions from others.

The business and technical development of the project struggled through and over many difficulties and disappointments for the first few years but with a constantly growing scale of operation; it was not until the fifth year of the work that the latter repaid what the organizers had spent upon it.

It is not the purpose here to enter upon the technical details of the inventions involved as the early history of these has already been published in THIS JOURNAL and quite fully abstracted elsewhere. ("The Electrical Precipitation of Suspended Particles," THIS JOURNAL, **3**, 542. *Engineering News*, Oct. 26, 1911, pp. 495–498. *The Engineering and Mining Journal*, Oct. 14, 1911, **92**, 763–764. *Mining and Scientific Press*, Aug. 26 and Sept. 2, 1911, **103**, 255–258, 286–289. *Rauch und Staub*, Apr., 1912, **2**, 187–195.) A further supplementary account and discussion was also given at the annual meeting of the American Institute of Mining Engineers last February.

Merely as an index to the practical significance which the work has already attained, suffice it to say that installations made under these patents have now been in commercial operation for over five years and the largest of these have been on a scale representing a construction cost of over $100,000 each. The first were in the far West but several are now in operation or under construction in and about New York City (see article by Schmidt, THIS JOURNAL, **4**, 719 and by Bradley, p. 908 of this issue, for instances).

By the time the work had thus reached a self-supporting basis, its significance was felt to have broadened to a degree which made its control by a local institution such as a single University inexpedient; the fullest success of such a movement is inevitably conditioned upon its being most broadly representative of the common interest of those whose coöperation and support it aspires to secure. Through Director J. A. Holmes, of the U. S. Bureau of Mines, who had taken a very helpful interest in the work, it was brought to the attention of the Smithsonian Institution nearly two years ago; the informal discussion which followed resulted last October in a formal offer of the patent rights to the Institution. The only condition qualifying this offer was that these patent rights should be given an adequate business administration and the proceeds be devoted to furthering scientific research.

In December last, after careful consideration and discussion with the prospective donors and under their hearty indorsement, the Board of Regents of the Smithsonian Institution adopted the following resolutions:

RESOLVED: That the Board of Regents of the Smithsonian Institution do not deem it expedient for the institution to become the direct owner of the proposed gift of royalty-bearing patents;

RESOLVED FURTHER: That the Board of Regents of the Smithsonian Institution decide that the Institution may properly accept a declaration of trust from the owners of the patents to hold and operate the same in the interests of the Institution, and to pay over to the said Institution the net profits therefrom.

The Board further authorized its Executive Committee and its Secretary, Dr. Charles D. Walcott, to coöperate with those from whom the offer had come in the organization of either a subsidiary or an independent board of trustees or directors to conduct the business side of the project.

In elaborating this plan, the organizers have tried to study carefully both the economic and academic needs which it was intended to subserve. The following are among the considerations which have perhaps had most to do in determining the form and policy of the new organization as finally constituted.

During the last few years, the rapid growth of engineering and technical education, coupled with a general awakening to the commercial importance of research in the industries, has brought about a persistent demand the world over for closer and more effective coöperation between the universities and technical schools on the one hand and the actual industrial plants on the other.

The value to both sides from such coöperation is to-day generally conceded, but as to the most expedient methods of its accomplishment opinions differ, and we are still in the experimental stage of working out the problem.

One solution which has been extensively applied

consists in universities and schools permitting and even encouraging the members of their teaching staffs to go into private consulting practice. Another form of coöperation is seen in the Industrial Fellowships recently established at several universities, through which their laboratories undertake the investigation of certain problems for individual commercial firms or organizations; the latter bear the expenses and receive the first fruits of the investigations, but under restrictions as regards final publication and use intended to justify the universities or technical schools in taking their part in the work.

While these and similar methods now in use bring about the desired coöperation, it has been felt by some that they are open to the objection of introducing too direct business relations between the academic institutions or the members of their faculties and individual financial interests. As still another alternative, intended particularly to meet to some degree at least this last objection, the Research Corporation has been organized.

Briefly stated, the Research Corporation is a board of administration, whose work is to guide the development of such patents as may be turned over to it, and finally market them, the net profits from all such business being devoted to scientific research "by contributing the net earnings of the corporation .....to the Smithsonian Institution and such other scientific and educational institutions and societies as the Board of Directors may from time to time select, in order to enable such institutions and societies to conduct such investigations, research and experimentation." Under this system, it will be noticed, a part at least of the financial returns of the scientific investigations of our academic laboratories automatically goes back to them for aiding further investigations.

But this represents only one side of the good which the plan aims to accomplish. Conservation has of late become a word to conjure with, and all manner of economic wastes are very properly receiving a too-long delayed attention. The men in our universities and colleges have been among the first and most effective in promoting the general conservation movement, yet there is what we may term an intellectual by-product of immense importance, a product of their own activities still largely going to waste. This is the mass of scientific facts and principles developed in the course of investigation and instruction, which through lack of the necessary commercial guidance and supervision never, or only after unnecessary delay, reaches the public-at-large in the form of useful inventions, and then often through such channels that the original discoverers are quite forgotten.

The Research Corporation was primarily intended to serve the ever-growing number of men in academic positions who evolve useful and patentable inventions from time to time in connection with their regular work and without looking personally for any financial reward would gladly see these further developed for the public good, but are disinclined either to undertake such developments themselves or to place the control in the hands of any private interest.

During the process of organization, however, it became evident that the class of donors of patents to the cause would by no means be limited to men in academic positions, but rapidly extended not only to private individuals outside the colleges, but even to large business corporations who often find themselves incidentally developing patents which overrun their own field of activities. Such patents are very apt to get pigeon-holed and come to actually stand in the way of true industrial progress, even though their owners may realize that development and use by others would indirectly benefit themselves. As an official of one of the large electrical companies put it—"Any extension of the use of electricity, or even power in general, is pretty sure eventually to mean more business for us through one department or another."

A procedure adopted by many men in academic and public positions in an attempt to bring various inventions before the public and at the same time prevent private monopoly has been to secure patents as a matter of record and then throw them open gratis to public use. This procedure received official recognition in the U. S. Patent Act of March 3, 1883, which authorizes the remission of all Patent Office fees to Government officials on patents bearing on their face permission for everyone in the country to use the invention without the payment of any royalty.

Practice has shown, however, that this does not accomplish all that had been hoped for it. A certain minimum amount of protection is usually felt necessary by any manufacturing concern before it will invest in the machinery or other equipment, to say nothing of the advertising necessary to put a new invention on the market. Thus a number of meritorious patents given to the public absolutely freely by their inventors have never come upon the market chiefly because, "what is everybody's business is nobody's business."

If some of these patents, on the other hand, were placed in the hands of such an organization as the Research Corporation, it could study the situation and arrange licenses under fair terms, so as to justify individual manufacturers undertaking the introduction of the inventions and at the same time it would be accumulating from the royalties funds for further investigations.

As to the details of organization, the Research Corporation was incorporated February 26, 1912 as a stock company under the laws of the state of New York, with its office at 63 Wall St., New York City, its declared purposes being:

(*a*) To receive by gift and to acquire by purchase or otherwise, inventions, patent rights and letters patent either of the United States or foreign countries, and to hold, manage, use, develop, manufacture, install and operate the same, and to conduct commercial operations under or in connection with the development of such inventions, patent rights and letters patent and to sell license or otherwise dispose of the

same, and to collect royalties thereon, and to experiment with and test the validity and value thereof, and to render the same more available and effective in the useful arts and manufactures and for scientific purposes and otherwise.

(*b*) To provide means for the advancement and extension of technical and scientific investigation, research and experimentation by contributing the net earnings of the corporation, over and above such sum or sums as may be reserved or retained and held as an endowment fund or working capital, and also such other moneys and property belonging to the Corporation as the Board of Directors shall from time to time deem proper, to the Smithsonian Institution, and such other scientific and educational institutions and societies as the Board of Directors may from time to time select in order to enable such institutions and societies to conduct such investigation, research and experimentation.

(*c*) To receive, hold and manage, and dispose of such other moneys and property, including the stock of this and of any other corporations, as may, from time to time, be given to or acquired by this Corporation in the furtherance of its corporate purposes, and to apply the same, and the proceeds or income thereof, to the objects specified in the preceding paragraph.

As practically all technical work under the Corporation's supervision will be done in coöperation with either industrial works on the one side, or school and college laboratories on the other, its expenses will be chiefly administrative, and were estimated for the first year at $10,000, the expectation being that after this it would be self-supporting. As a margin for unforeseen contingencies, the capital was placed at $20,000, divided in 200 shares, of a par value of $100 each, and issued under the condition that "no dividends shall be declared or paid thereon, and the entire net profits earned by said capital stock shall be applied to or expended for the aforesaid purposes." All stock issued is also under an option to the Corporation by which the latter may, at any time, through its Board of Directors, repurchase it at par, and the stock cannot be otherwise sold, without first notifying the Board and allowing the latter an opportunity to exercise this option.

Of the total 200 shares, 101 have thus far been issued and their par value paid into the Corporation's treasury as working capital. This stock is held in lots of from three to ten shares by the following list of stockholders:

Edward D. Adams, of the Deutsches Bank, New York.

Cleveland H. Dodge, of the National Bank and Farmers Loan and Trust Company, New York.

James Douglass, President of Phelps, Dodge & Co., President of El Paso & S. W. R. R., New York.

T. Coleman du Pont, formerly President of the du Pont Powder Co., Wilmington, Del.

Frederick A. Goetze, Dean of the Faculty of Applied Science, Columbia University, New York.

Elon Huntington Hooker, President of the Development & Funding Co., New York.

Hennen Jennings, of the Sea Board Air Line.

Charles Kirchhoff, Past President American Institute of Mining Engineers, New York.

Benjamin B. Lawrence, Consulting Mining Engineer, New York.

Arthur D. Little, President American Chemical Society, Boston.

Thomas C. Meadows, Vice-President International Agricultural Corporation, New York.

H. C. Perkins, President Oriental Consolidating Mining Co., New York.

Charles A. Stone, of Stone & Webster, Boston.

James J. Storrow, of Lee, Higginson & Co., Bankers, Boston.

Elihu Thomson, of the General Electric Co., Lynn, Mass.

Henry R. Towne, of Yale & Towne, President of the Merchants' Association, New York.

Charles D. Walcott, Secretary of the Smithsonian Institute, Washington, D. C.

The Directors, who need not be stockholders, are 15 in number, seven constituting a quorum, and are elected for a period of three years, one-third going out each year. They in turn elect each year an executive committee of five, of which three constitute a quorum. The present personnel of the administration is as follows:

OFFICERS:

Vice-President,	Charles D. Walcott
Secretary,	Lloyd N. Scott
Treasurer,	Benjamin B. Lawrence
Assistant Treasurer,	Columbia Trust Co.

DIRECTORS:

To serve until 1913.

T. Coleman duPont	Charles A. Stone
Arthur D. Little	Elihu Thomson

M. B. Philip

To serve until 1914

Frederick A. Goetze	John B. Pine
Benjamin B. Lawrence	Lloyd N. Scott

Charles D. Walcott

To serve until 1915

Thomas C. Meadows	Hennen Jennings
Elon H. Hooker	Charles Kirchhoff

James J. Storrow

EXECUTIVE COMMITTEE:

Frederick A. Goetze, *Chairman*

Benjamin B. Lawrence	Elon H. Hooker
Charles D. Walcott	Arthur D. Little

John B. Pine, *Counsel*
Linn Bradley, *Engineer*

It is not proposed to fill the offices of President and Manager until the work of the Corporation is well under way and the permanent demands and responsibilities on these officers can be better estimated, their duties devolving in the meantime upon the Vice-President, Chairman of the Executive Committee and Engineer.

The present organization is not considered as necessarily permanent in all its details but was deemed the most simple and generally expedient for carrying out the initial stages of this experiment in economics, at least until it should have earned a safe working surplus of its own and demonstrated its ability to produce a substantial permanent revenue. It will then devolve upon the Board of Directors to decide upon a definite policy for the ultimate control of the Corporation. This may be done by exercising the option to repurchase all outstanding stock at par and then proceed to redistribute the same, as for example, by turning the whole over to the Smithsonian Institution, or perhaps better still by dividing it among a number of universities and similar institutions. This, of course, does not mean that the particular institutions so selected would thereby acquire any more direct claim on the profits of the corporation than others, since the stock is non-dividend bearing,

but merely that they would become trustees responsible for the election of Directors who would give the Corporation a business administration, thoroughly practical but conforming to the ideals implied by its objects and associations.

The terms under which each new patent shall be acquired by the Corporation are entirely in the hands of the Board of Directors, but at least for some time to come it is probable that only such patent rights will be primarily considered as are offered freely, without restrictions as to mode of administration or obligation of any financial return from the Corporation, as present indications are that the latter will find itself well occupied even by these offers alone.

The Board has authority to purchase patents where this may appear as good business policy, which may quite conceivably occur from time to time in rounding out fields in which it has already embarked. Contracts with owners of patents for administrating the same on a profit-sharing basis will probably not be considered, chiefly owing to the unforeseen complications which it is easily possible, not to say certain, that such agreements would eventually lead into as the further developments of different interests began to overlap.

A much simpler, safer and more expedient procedure appears to be for the patentee to retain if he so chooses complete title and control of his patent in certain geographical territory, while assigning the same in other territory entirely unencumbered to the Corporation. Any development which the latter can give it will then automatically enhance the value to both.

This procedure is well illustrated in the case of the first patents to come into the possession of the Corporation, *viz.*, those referred to above as initially offered to the Smithsonian Institution itself. The owners of these at the time of their original offer had already spent considerable time and money in their development, but from the outright sale of their foreign rights and the rights of six western states (California, Oregon, Washington, Idaho, Nevada, and Arizona), together with a license for the one industry of Portland Cement manufacture throughout the whole United States, they felt adequately remunerated for their work and financial risks, and were willing to turn over all remaining United States patent rights as a nucleus for the experiment in economics which the Research Corporation represents. Together with this there came to the Corporation a 10 per cent. interest in the net profits of the parties who purchased the rights for the Western States and for the cement industry, while incidentally growing out of the negotiations on the foreign rights, another set of valuable patents has come to the Corporation from Mr. Erwin Moeller, of Germany, which emphasizes in a most practical way the fact that academic organizations, and particularly the Smithsonian Institution, are international in spirit, and so recognized by scientific men the world over, presenting at once a nucleus from which may well be developed many activities leading toward world consciousness, coöperation and peace.

The present movement, as stated, had its inception on the far western edge of this continent in very unpretentious beginnings, but has already overrun national borders both in the character of its work and the personnel of its supporters. It is a question which should peculiarly interest this Congress as to how far and in what way international coöperation can best be assured in such activities which, from their very nature and aims, should from the outset transcend political boundaries and national pride and be treated by one and all from a standpoint as broad as humanity itself. It was with this in mind that the present paper has been presented, not so much as a record of present achievement, as to stimulate discussion and coöperative effort toward ever wider and more effective activities in this most promising field.

F. G. Cottrell.[1]

ORIGINAL PAPERS

A STUDY OF THE VARIATIONS OF THE PHYSICAL AND CHEMICAL PROPERTIES OF RED LEAD.

By O. W. Brown and A. R. Nees.

Received Aug. 2, 1912.

Red lead is an oxide having the empirical formula Pb_3O_4. The chemical composition and physical properties vary within wide limits, depending upon the method of manufacture and the nature of the material from which it is made. Two distinct modifications of this oxide are known in commerce: ordinary red lead or minium, and orange mineral. The exact difference between these two modifications is not clearly understood. It is not our purpose, however, to enter into a discussion of this. What we do want to do, is to point out some of the variations in chemical and physical properties of ordinary red lead and the factors which control these variations.

In order to make the subsequent discussion clear, a brief résumé of the various processes employed for the manufacture of red lead will be given. Companies which make white lead burn their "off color" white lead to minium. In a second process molten lead is rabbled in a reverberatory furnace. The greenish yellow oxide, or massicot as it is called, thus obtained is ground and separated from the particles of metal by air or by levigation. This oxide is then burned to red lead. In some processes the levigation is dispensed with and the massicot is alternately ground and heated until conversion to red lead is complete.[2]

In another method[3] litharge is first made from the metal, and tapped from the furnace in a fused condition. After being allowed to cool it is ground and

[1] The substance of this article was presented in an address before the Eighth International Congress of Applied Chemistry, New York, September, 1912.

[2] W. Eckford, Brit. Pat. 25,256, Dec. 4, 1908, and 15,423, July 1, 1909. *J. S. C. I.*, **29**, 166.

[3] Hoffman's "Metallurgy of Lead," 4th Ed., pp. 15 and 16.

burned to red lead. Two modifications of litharge may be obtained by this process. If the fused litharge is allowed to cool *slowly*, a so-called "red" litharge is obtained; but if it is cooled *rapidly* by allowing it to flow onto water-cooled iron plates a "yellow" litharge is obtained. Both varieties are used for making red lead. Processes are also in use in which atomized lead, after previous treatment with water etc., is converted into red lead. The "Nitrate Method" in which sodium nitrate is reduced to nitrite by means of metallic lead is also in use. The oxygen from the sodium nitrate oxidizes the lead to litharge or even to red lead. Several other methods have been patented and are in use.[1] The red lead obtained by these various processes differs widely in physical and chemical properties. In most cases it is easy to determine the method of manufacture of a commercial red lead by means of a microscopic examination.

A review of the literature shows that little work has been done toward determining the conditions best suited for the production of a red lead having given chemical and physical characteristics. J. Milbauer has made a study of the factors which affect the oxidation of litharge to red lead. The result of his work is given in a series of papers on "The Physical Chemical and Technical Studies of Minium."[2] Milbauer carried out his experiments in a rotatable tube through which air or oxygen was passed. He found that the rate of oxidation was independent of the rate of rotation of the tube up to a certain limit. When the rate of rotation exceeded thirty revolutions per minute, small pellets were formed, thus reducing the surface exposed, and hence the rate of oxidation. The presence of moisture or preheating of the air or oxygen had no effect on the rate of oxidation. The surface being sufficiently great, the only things which affect the rate of oxidation are the temperature and partial pressure of the oxygen. For example, in one of Milbauer's experiments lead oxide heated at twelve atmospheres pressure for one hour contained 60 per cent. red lead, while in pure oxygen at the same temperature and pressure only a few minutes were required for the oxidation to take place. At atmospheric pressure about fifteen hours are required to effect the same degree of oxidation.[3] He has pointed out that the source of the litharge has a greater influence upon the rate of oxidation than the size of the particles.[4]

Milbauer concluded from his experiments that under 450° C. no red lead is obtained from litharge, the product always being brown in color. From 450° to 550° C. the product was red. The best results were obtained at about 470° C. He also states that red lead made from lead carbonate is reduced at this temperature. These statement are not all in accordance with our own experimental results, as will be shown later. He says that small amounts of impurities in the litharge have a very marked influence upon the rate of oxidation; that nitric acid and ammonia vapors reduce the rate of oxidation to about one-third and one-seventh, respectively, of its original value; that small amounts (about 0.1 per cent.) of lead nitrate and of sodium nitrate slightly accelerate the rate of oxidation; that the presence of 0.1 per cent. of lead nitrate gives the product a fine pink color and that a similar amount of NaOH gives an intense red.[1] He found that an increase of ten degrees C. in the reaction temperature multiplied the rate of reaction by only about 1.05, as compared with the usual doubling or trebling the speed of an ordinary chemical reaction, for an increase of ten degrees. From this fact he concluded that the change is a physical rather than a chemical one, and is to be explained by the theory of solid solutions advanced by Horstmann.[2] In another paper Milbauer[3] states that decomposition is less rapid in oxygen than in air, more rapid in carbon dioxide than in either air or oxygen, and most rapid in a vacuum.

It should be borne in mind that in all of these studies of the rate of oxidation, Milbauer used litharge as a starting material. Litharge is much more difficult to oxidize to red lead than normal or basic lead carbonate or lead hydroxide. In the papers referred to above, Milbauer gives 470° C. as the temperature best suited for the oxidation of litharge to red lead. He also points out that at a temperature only five degrees above this, red lead made from lead carbonate is rapidly reduced. We find that reduction does not take place at this temperature and that red lead containing more than 30 per cent. lead peroxide (about 87 per cent. Pb_3O_4) can be obtained from lead carbonate at 500° C.

In the experiments which we have carried out, not only the effect of temperature upon the rate of oxidation of different starting materials but also the physical and chemical properties of the red lead formed from the different substances under different conditions of temperature have been studied. We have studied red lead made from litharge, lead hydroxide, white lead, lead sponge, metallic lead and lead tartrate. A microscopic examination of each sample was made. The real and apparent density and content of lead peroxide were determined. The relative plasticity of the different samples when made into putty-like paste with water was also noted. Besides the samples prepared in the laboratory we have examined a large number of samples of commercial red lead and litharge manufactured by different companies.

In the study of the rates of oxidation the "Rotary Electric Laboratory Furnace," to be fully described by us in another paper, was used. A slow current of air was forced through the furnace; the rate of flow of the air through the furnace seemed to have little effect upon the rate of oxidation. Three porcelain balls about an inch in diameter were kept in the rotating jar, for the purpose of keeping the charge well stirred. The rate of rotation was about nineteen to twenty revolutions per minute.

[1] E. L. Burton, Fr. Pat. 351,812, Feb. 28, 1905. *J. S. C. I.*, **24**, 892.
[2] J. Milbauer, *Chem. Ztg.*, **33**, 522.
[3] J. Milbauer, Eng. Pat. 25,757, Nov. 18, 1911.
[4] J. Milbauer, *Chem. Ztg.*, **34**, 1341–42.

[1] J. Milbauer, *Chem. Ztg.*, **33**, 950.
[2] Hortsmann, *Z. physik. Chem.*, **6**, 7.
[3] J. Milbauer, *Chem. Ztg.*, **34**, 138–40.

The plan of the furnace is shown in Fig. A. *D* and *E* are heating coils, *F* is the rotating jar, and *B* is the outer jacket. The air follows the course indicated by the arrows. In this furnace the method of heating insures that the rotating jar and its contents will be heated to the same temperature and that a pyrometer inserted in the jar will record the true temperature of the charge.

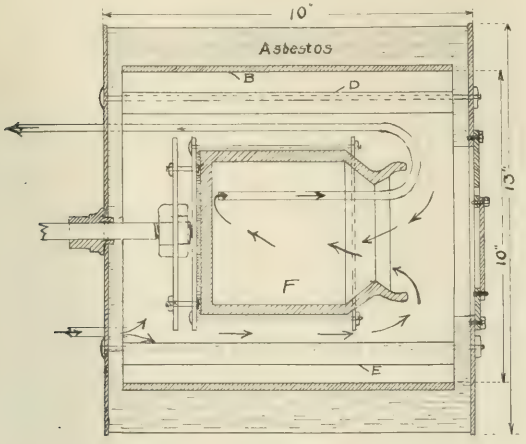


Fig. A.

In the case of white lead the rate of oxidation was determined at temperatures ranging from 350° C. to 500° C.

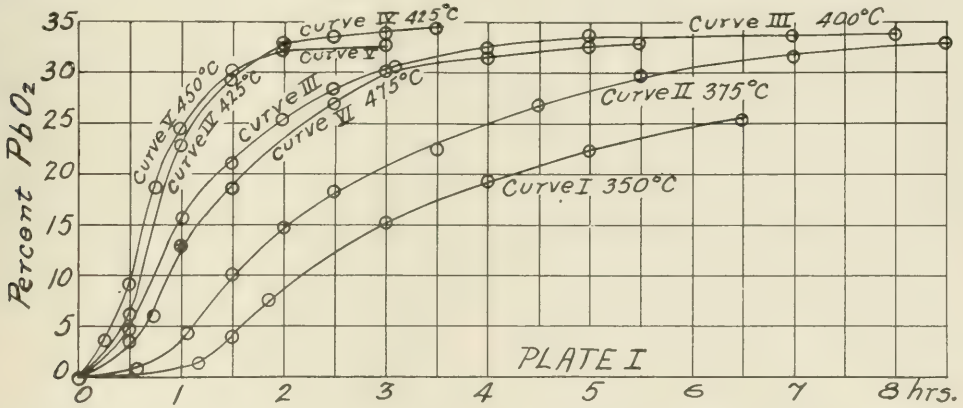
During each run small samples were taken from time to time and analyzed for lead peroxide. (The amount of lead peroxide is a measure of the degree of oxidation. Red lead of theoretical composition corresponding to the formula Pb_3O_4 contains 34.89 per cent. lead peroxide.) The effect of temperature is very strikingly illustrated by the curves on Plate I, in which the percentage of lead peroxide is plotted as ordinate against the time as abscissa. In each case it will be noticed that the curve rises slowly at first, then more rapidly, and again very slowly toward the end, thus dividing it into three distinct parts. The slow rise at the beginning is due to the decomposition of the white lead. Oxidation can proceed only after the CO_2 is driven off. The steep part of the curve represents the real rate of oxidation before a condition of equilibrium is approached. The straight part of the curve at the end, especially noticeable at the higher temperature, represents the state of equilibrium between the red lead and air at that temperature.

The rate of oxidation of white lead at different temperatures is illustrated by the curves on Plate I. Oxidation takes place most rapidly at 425° to 450° C. At 450° C. a state of equilibrium between air and red lead is reached at about 32.7 per cent. PbO_2, while at 425° C. the state of equilibrium is above 34 per cent PbO_2. Above 450° the rate of oxidation decreases. This is illustrated in Curve VI on Plate I, which shows the progress of oxidation at 475° C. At 500° C. oxidation is much slower, eight hours being required to obtain a red lead containing 31.50 per cent. of PbO_2. It was not possible to obtain a smooth curve at this temperature since the rate of oxidation is not uniform.

In Plate IV the percentage of PbO_2 is plotted against the temperature, the time being the constant factor. The percentage of PbO_2 in the product at the end of three hours and two hours at the various temperatures is shown in Curves I and II, respectively. These curves clearly indicate that the rate of oxidation of white lead is a maximum at a temperature of 425° C. to 430° C.

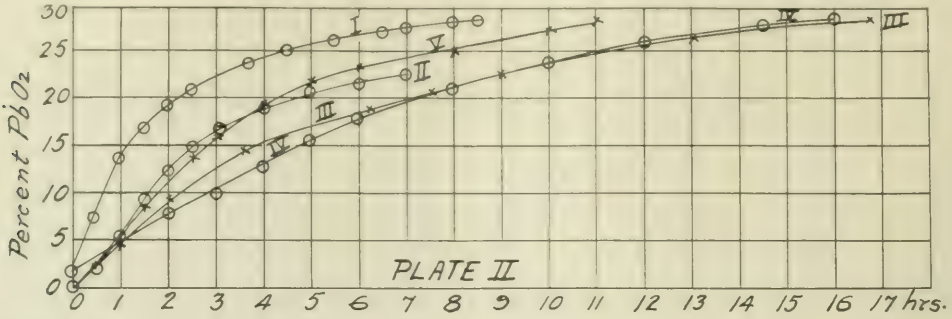
The rate of oxidation of sublimed litharge[1] at 425° C. is shown by the curve on Plate III. In this case equilibrium was reached at 33.72 per cent. PbO_2. This composition was maintained during five hours heating.

In Curve I on Plate II the rate of oxidation of a red litharge at 450° is shown, while that of a litharge of the yellow modification is shown in Curve II. It will be noticed that the yellow litharge oxidized much more slowly than the red variety. If litharge is treated with water, dilute tannic acid, or glue solution, the rate of oxidation is materially decreased. Water and tannic acid solution have about the same effect, while glue solution has less retarding influence.



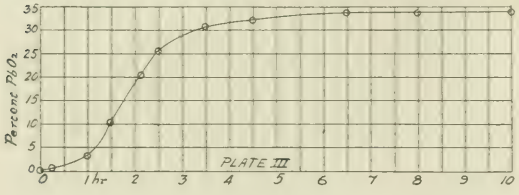
[1] Sample furnished by Picher Lead Company.

The untreated red litharge was converted to red lead containing 28.01 per cent. lead peroxide in eight hours, while sixteen hours were required to obtain a red lead of like composition after the litharge had been treated with water or tannic acid solution. Eleven

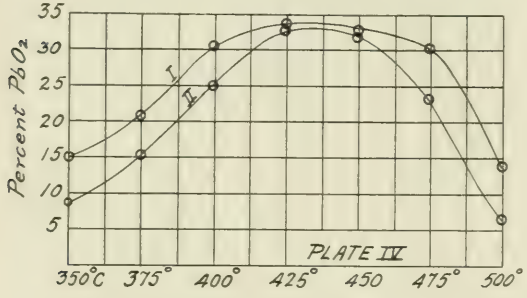


hours were required in the case of litharge treated with glue solution. These facts are brought out in Curves III, IV, and V, respectively. A like treatment affected the rate of oxidation of yellow litharge to about the same extent.

We did not make an extended study of the effect this class of substances has upon the rate of oxidation



and the results stated above were noted in connection with a series of experiments carried out for a different purpose. However, it is of interest to know that water and certain colloidal solutions have a very marked effect upon the rate of oxidation. The specific gravity and apparent density are also slightly influenced by these additional agents and by the single treatment with water, as will be shown later.



It is to be noted that other litharges which do not appear to have been fused during the process of manufacture require a much longer time for oxidation to red lead.

Red leads made from lead hydroxide, lead sponge, pig lead, atomized lead, and lead tartrate were also studied.

The lead hydroxide was prepared by the electrolysis of $NaNO_3$ solution, using lead electrodes. The hydroxide was thoroughly washed, dried and ground in a pebble mill. It was found impossible to remove all of the nitrate even by the most thorough washing. J. Milbauer has pointed out that the presence of nitrates is not objectionable. The presence of the nitrates in this instance seemed to reduce the rate of oxidation. Oxidation did not begin at all until all of the nitrates were broken down. Hydroxide which has been exposed to the air for several weeks is more easily oxidized than freshly prepared hydroxide, due to the fact that it is partially converted to carbonate. The old hydroxide can be oxidized to red lead of almost theoretical composition at 450° C. in about five hours, while the fresh material requires twice as long as the same temperature. The red lead prepared from lead hydroxide is amorphous as shown in Fig. 19 and has a slight pinkish tint due to the nitrates which were present in the hydroxide. The specific gravity is low, varying from 8.46 to 8.93, depending upon the temperature at which it was made.

The lead sponge used in these experiments was obtained by two methods: (1) by electrolyzing a hot, saturated solution of litharge in caustic soda, using lead electrodes, and (2) by deposition from an aqueous lead acetate solution acidified with acetic acid, using a large lead anode and a small lead cathode. The sponge thus obtained was carefully washed and dried at 50° to 60° C. It was then repeatedly moistened with water and dried. This exposure to air and water partially converts the sponge to hydrated oxide and carbonate. The crystals of the acetate sponge disintegrate much more readily upon exposure to air and moisture than do those from the alkali bath, due probably to the acetic acid present.

Both varieties of sponge yield an excellent quality of oxide of a fine deep red color. A microscopic examination shows the product to be made up largely of crystals mixed with some fine amorphous particles. In general, the specific gravity is about that of a red lead made from ordinary litharge. The rate of oxidation of both the acetate and alkali lead sponge is lower than that of fused litharge and more rapid than that of a litharge which has not been fused;

however, the alkali sponge oxidizes more rapidly than that from the acetate bath.

It is interesting to note that a red lead of lower specific gravity than any so far obtained was produced from sponge taken from the alkali bath. The sponge was almost free from crystals and was rapidly oxidized to nearly theoretical composition. It had a specific gravity of 8.32. All other samples prepared from sponge had a much higher specific gravity; however, the samples of sponge from which they were made were more crystalline and not amorphous.

Samples of red lead were also prepared from ordinary metallic lead and from atomized lead.[1] It was not possible in any experiment to oxidize the metal directly to red lead. Various temperatures from just above the melting point (326°–327°) up to 500° C. were tried. The metal first fuses, then becomes granular, due to the rotation of the furnace. The finer particles are entirely converted to red lead while the larger ones merely become coated over with the oxide, making further oxidation very difficult. When the product reached this stage it was removed from the furnace and ground. The finer particles were separated by levigation, the residue was roasted again, and the grinding and levigation repeated The second treatment left only a small residue of unoxidized lead which was discarded. The finer portion, which was a reddish brown color, was then put into the furnace and further oxidized. Only a short time (three to four hours at 430° to 450° C.) was required to convert the material into a brilliant, amorphous red lead.

The atomized lead was treated in the same manner as ordinary metal and seemed to possess no advantages over it. The atomized lead, of course, did not fuse since the particles become quickly coated with oxide.

By means of the microscope one is able to distinguish different modifications of red lead. In general, there are two distinct modifications, amorphous and crystalline. Some commercial red leads are entirely amorphous, some are entirely crystalline, while others are a mixture of the amorphous and crystalline modification. So far as we have been able to determine, red lead has no definite crystalline form of its own but retains the form of the substance from which it is made. The fact will be made clearer by an examination of the photo-micrographs. All of the oxides shown in the photo-micrographs are magnified to 215 diameters.

A study of the effect of temperature, time of heating, chemical composition, and physical modifications upon the specific gravity was also made. Considerable difficulty was encountered in obtaining accurate determinations of the real specific gravity. The method finally adopted was to use 15 cc. and 20 cc. graduated, glass-stoppered flasks, for pyknometers. Alcohol was used in the pyknometers instead of water. Water is not suitable because it does not wet the particles of red lead thoroughly and because a portion of the sample always floats, due to the high surface tension of the water. Ordinary 95 per cent. alcohol was treated with silver oxide and caustic soda for several days and then distilled. This treatment removes the aldehydes and other impurities. Before distillation, a small amount of water was added and only that part of the distillate reserved for use which had the composition of the constant boiling mixture of alcohol and water. This treatment gives a pure alcohol, which does not appreciably change in density upon exposure to air. The alcohol thus prepared was put into a vacuum desiccator and the pressure reduced to about 3 cm. of mercury for two hours. The density of the alcohol was then carefully determined by means of the pyknometers mentioned above —the exact capacity of the pyknometers having been determined by means of distilled water at a known temperature.

Since a long series of determinations was to be made and since alcohol has a relatively high coefficient of expansion it was necessary to work under conditions of constant temperature. Twenty-five degrees C. was chosen as being the most convenient. For this purpose an ordinary electrically operated thermostat was used. The temperature remained constant to within less than 0.1° C.

The determinations were carried out in the following manner: Ten to fifteen grams of the sample are introduced into the weighed pyknometer and the total weight carefully made. The flask is filled about half full of the standard alcohol and thoroughly shaken. It is then placed in a vacuum desiccator and the pressure reduced to about 4 cm. of mercury for two to three hours. This treatment is necessary in order to remove the small air bubbles which adhere to the particles of red lead. The flask is then filled accurately to the mark with more alcohol (while the temperature is maintained at 25° C.) and weighed. The specific gravity is calculated according to the following formula,

$$D = \frac{d\,w}{w_1 - (W - W_1)},$$

where d = density of the alcohol, w = weight of the sample, w_1 = weight of alcohol required to fill flask, W = total weight of bottle + sample + alcohol, W_1 = weight of bottle + sample.

Close attention to details is necessary in order to obtain accuracy in these determinations. After each determination the pyknometers should be rinsed with alcohol and then with nitric acid, which in presence of the alcohol quickly dissolves all of the red lead remaining. They are successively washed with water, alcohol, and finally with ether, the latter being removed by a current of air.

The specific gravity of red lead is found to vary from 8.32 to 9.16. The lower value was obtained for a red lead made from lead sponge. The sample was slightly crystalline, as is shown by Fig. 7. The higher value was found for a commercial red lead (see Fig. 8) which appears from the photo-micrograph to be a mixture of the crystalline and

[1] The atomized lead was procured from The Chemical Process Co., of New York City.

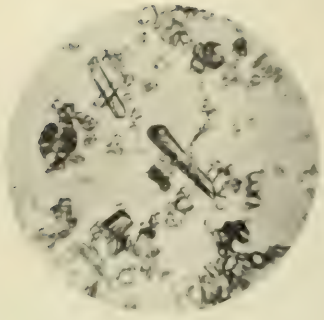


FIG. 1.
Lead Tartrate Crystals.

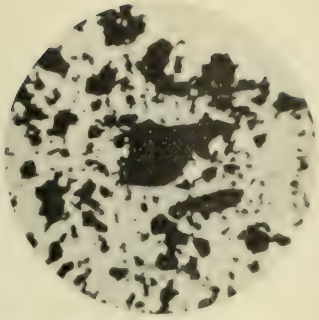


FIG. 5.
Red Lead made from the Lead Sponge shown in Fig. 6.

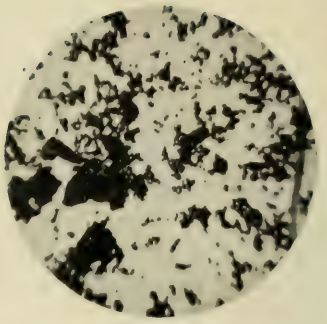


FIG. 8.
A commercial Red Lead, partly crystalline and partly amorphous.

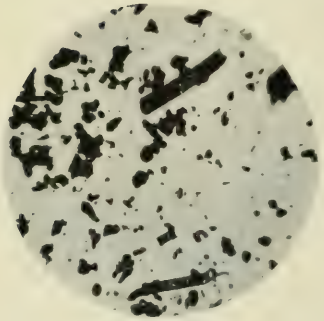


FIG. 2.
Red Lead made from Lead Tartrate.

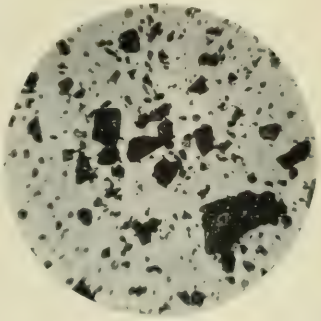


FIG. 6.
Lead Sponge from an Acetate Bath.

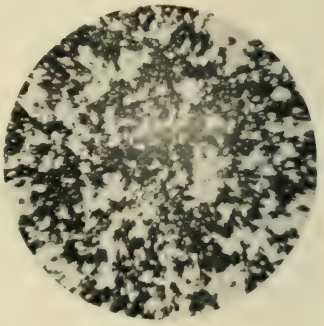


FIG. 9.
An amorphous commercial Red Lead.

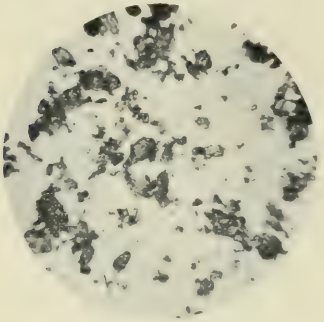


FIG. 3.
A commercial "Red" Litharge.

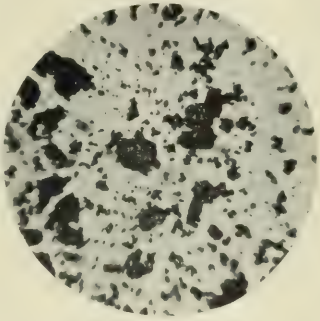


FIG. 7.
Red Lead made from Alkali Sponge.

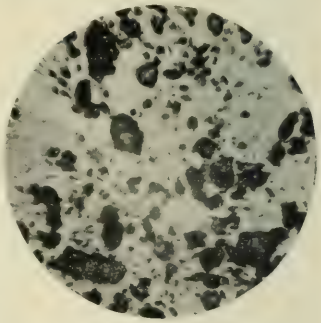


FIG. 10.
A Litharge made from the Red Lead shown in Fig. 9.

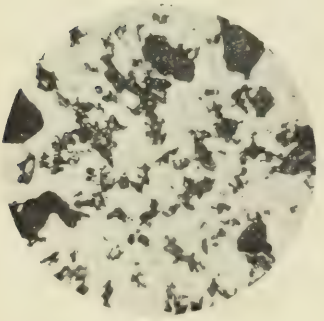


FIG. 4.
A commercial Red Lead made from the Litharge shown in Fig. 3.

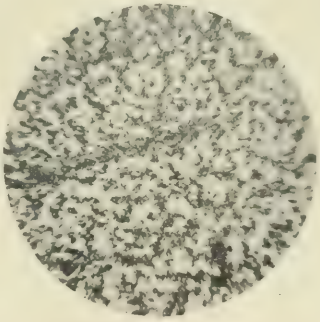


FIG. 11.
Sublimed Litharge.

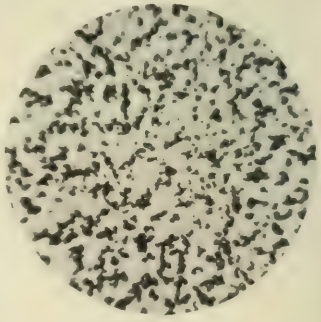


FIG. 12.
Red Lead made om Sublimed Litharge

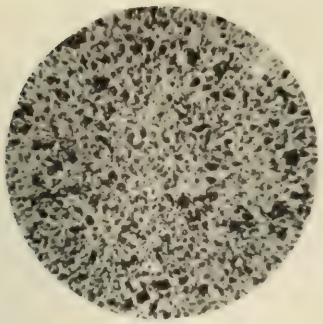


FIG. 13.
Red Lead made from White Lead.

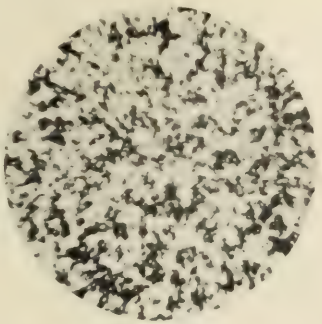


FIG. 14.
Red Lead made from White Lead.

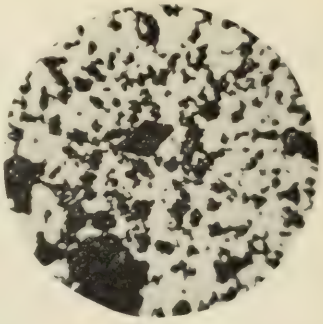


FIG. 15.
Red Lead made from White Lead that has been reduced to Litharge and then re-oxidized.

amorphous modifications In general, amorphous samples prepared in the laboratory and found in commerce have a specific gravity of from about 8.66 to 8.9, while the crystalline varieties have a higher real density. This generalization is not strictly true in all cases. In the following table the specific gravity of various samples prepared in the laboratory as well as a number of commercial samples is given. The data in Table I shows that the specific gravity of red lead made from white lead varies from 8.66 to 9.12. This variation seems to be a function of the temperature, the time of heating, and the chemical composition. In general, the higher the temperature at which oxidation takes place, other factors being constant, the higher the specific gravity. The more nearly the sample approaches the formula Pb_3O_4, the lower is the specific gravity.

The specific gravity also increases slightly with time of heating. For example, sample B–C–4, heated at 400° C. for four hours, contained 33.41 per cent. PbO_2 and had a specific gravity of 8.82, while sample B–D–10 heated at the same temperature for eight hours and containing 33.73 per cent. PbO_2 had a specific gravity of 8.90. The effect of temperature on the specific gravity is shown very strikingly in the case of samples B–V and B–V–K. Sample B–V was made from white lead, at about 425° C. It contained 32.97 per cent. lead peroxide and had a specific

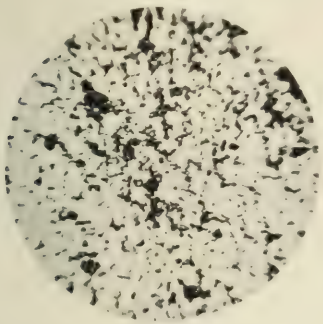


FIG. 16.
Red Lead made from Atomized Lead.

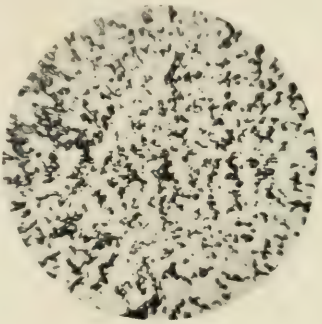


FIG. 17.
Red Lead made from Metal.

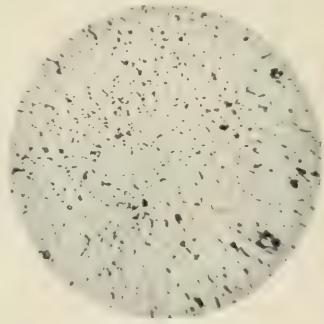


FIG. 18.
An amorphous Red Lead (See Fig. 9) ground for 50 hours.

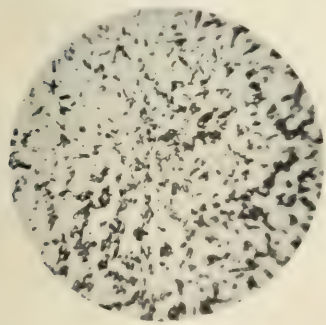


FIG. 19.
Red Lead made from Lead Hydroxide.

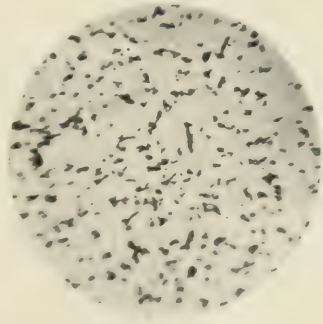


FIG. 20.
Lead Carbonate from Sodium Methyl Sulphate Bath.

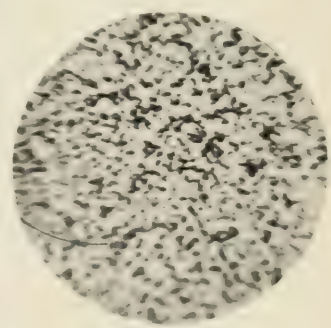


FIG. 21.
Red Lead made from the Carbonate in Fig. 20.

gravity of 8.66. It was then completely reduced to litharge by heating to a temperature a little above 500° C., after which it was reoxidized to red lead at 425° C. The rate of oxidation in this case was very slow. About forty hours were required to bring the per cent. of peroxide up to its former value. The specific gravity was now found to be 9.12 instead of 8.66. The same experiment was tried in other cases and the same effect was always observed; in most instances the effect was much more marked than in the above example. From Fig. 15 it is seen that partial crystallization takes place when the sample is heated to 500° or above. Indeed we are no longer dealing with a red lead made from white lead but one made from litharge. Any amorphous red lead will, if heated to 525°, be reduced to litharge. The litharge thus obtained will not be amorphous but crystalline. Fig. 10 shows a litharge made by heating the amorphous red lead shown in Fig. 9. A comparison of the two figures will bring out the striking physical change which has taken place. The objection may be raised that the particles of litharge do not seem to conform to any of the crystallographic forms, and that, strictly speaking, they should not be called crystals. It is true that only in very rare cases do perfect crystals appear, as, for example, in Fig. 15. However, the shape of the particles indicate that they are fragments of crystals.

TABLE I.

SAMPLE.	STARTING MATERIAL.	Temp. C.	Hours heating.	Per cent. PbO_2.	Specific gravity.	Apparent density.	REMARKS.
B–E–8	White lead	425°	3½	34.42	8.69		
B–E–4	"	425°	2	22.72	8.73		
B–A–9	"	350°	6½	25.28	8.78		
B–O–10	"	400°	8	33.73	8.90	17.11	
B–C–2	"	400°	2½	28.73	9.02		
B–C–4	"	400°	4	33.41	8.82		
B–B–6	"	375°	3½	22.39	8.91		
B–B–10	"	375°	8½	33.06	8.74	19.82	
B–F–4	"	450°	1	24.33	9.07		
B–F–8	"	450°	3	32.70	8.91		
B–F–6	"	450°	2	32.27	8.89		
B–G–11	"	474°	5½	33.06	9.05	19.03	
B–I–11	"	500°	8	31.50	9.04	27.30	
B–K–3	"	425°	2½	30.52	8.81	10.34[1]	Made from lead carbonate prepared electrolytically in a lead methyl sulphate bath.
B–V	"	425°		32.97	8.66)		Sample B–V reduced to litharge at 525°
B–V–K	"	425°		32.49	9.12)		and reoxidized to form B–V–K.
F–A–6	Lead hydroxide	425°	6		8.46	23.31	
F–VIII	"	445°	5½		8.92		
F–IV	"	400°	15	83.53	8.58		
F–III	"	450°		29.24	8.93		
F–V	"	400°		34.45	8.55		
H–A–9	Lead sponge	450°	6½	28.10	8.96	34.05	Alkali sponge.
H–I	"	400°	9	34.15	8.32		Acetate sponge.
H–III–14	"	400°	22	28.36	8.78		Alkali sponge.
H–V–6	"	400°	9	26.04	9.04		"
H–VI–6	"	440°	9	23.25	9.10		"
K–A–7	Sublimed litharge	375°	7	25.30	9.04		
K–B–13	"	425°	11½	32.72	9.02	17.16	
M–A–17	Litharge	400°	15	14.20	9.24	28.06	
M–E–15	"	450°	16¾	28.59	8.78	24.41[1]	Red modification treated with water.
M–F–17	"	450°	16	28.30	8.87	21.20	Red modification treated with tannic acid solution.
M–G–11	"	450°	11	28.24	8.87	20.62[1]	Red modification treated with glue solution.
M–H–12	"	450°	8½	28.01	8.80	19.22[1]	Red modification (untreated).
M–I–11	"	450°	7	22.80	8.94	25.88	Yellow modification (untreated).
C–C–C	Atomized lead	425°–450°		30.99	8.89	29.2	
R–PP	Metal	425°–450°			9.02		
S–R–L–50				32.41	8.83	24.41	Amorphous commercial red lead, ground fifty hours.
S–R–L				32.41	8.81	18.83	Same as above. Not ground.
P–S–L					9.26	7.32	Sublimed litharge.
A–R–				26.93	9.16	30.87	A commercial red lead.
A–Y					9.36	30.83	A commercial litharge.
S–L					9.33	36.09	A commercial litharge.
R–R–L				27.05	9.06	22.43	A commercial red lead.
R–I–R				25.18	8.87	19.11[1]	A commercial red lead.
R–I–L					9.19	26.83[1]	A commercial red litharge.
R–I–L–W					8.73		Same as R–I–L treated with water.
R–I–L–T					8.95		Same as R–I–L treated with tannic acid.
R–I–L–G					8.95		Same as R–I–L treated with glue solution.
R–D–L					9.32	31.54[1]	Yellow litharge from fused litharge.
R–D–R				23.58	8.92	22.79[1]	Red lead made from R–D–L.
L–S–R					9.45	32.76	Litharge made from amorphous red lead (S–R–L).
E–R				25.04	8.96		A commercial red lead.
S–L–50						29.81	Same as S–L ground fifty hours.

[1] Determined with Scott apparatus, as modified by Dr. Schaffer.

The marked change in specific gravity noted in the above experiments clearly indicates that a permanent physical change has taken place and that after an amorphous red lead has been heated above the reduction temperature and again oxidized to its original peroxide content, it exists as a different modification, having different physical properties.

An amorphous red lead formed at temperatures just below the reduction temperature (see B–I–11 and B–G–11, Table I) also has a high specific gravity, which goes to show that the transformation begins below the reduction temperature.

However, the fact that a red lead is crystalline does not necessarily mean that it has a high specific gravity. On the other hand, a red lead made from lead sponge from a sodium hydroxide bath and having a slightly crystalline character, had a specific gravity of 8.32, which is the lowest value we have observed in any case. (See H–I in Table I, Fig. 7.) Certain commercial red leads, for example R–I–R, Fig. 4, made from a fused litharge, also have a specific gravity which is comparable to that of the amorphous red lead found on the market or made in the laboratory. It would appear from these facts that some change other than of mere physical form is responsible, in part at least, for the variations in specific gravity.

This phenomenon may be explained on the basis of Wades'[1] theory concerning the polymerization of lead compounds. He assumes that litharge, for example, does not have the simple formula PbO, but a complex formula, Pb_xO_x. He also assumes that when PbO is converted to red lead it is not converted molecule by molecule, but that the oxidation takes place gradually and uniformly through the whole mass, whenever the conditions of oxidation are favorable. For example, if we assume the formula of litharge to be $Pb_{12}O_{12}$ the oxidation, according to the theory, takes place in the following manner:

$Pb_{12}O_{12} = 12PbO$;
$Pb_{12}O_{13} = 11PbO + PbO_2$;
$Pb_{12}O_{14} = 10PbO + 2PbO_2$;
$Pb_{12}O_{16} = 8PbO + 4PbO_2 = 4Pb_3O_4$;
$Pb_{12}O_{18} = 6PbO + 6PbO_2 = 6Pb_2O_3$.

The molecule of litharge is not converted directly to Pb_3O_4 but passes through successive stages of oxidation and may even, in some cases, pass as far as the sesquioxide Pb_2O_3.

The application of this theory to the observed variations in specific gravity is at once obvious. Let us assume that the formula of a red lead made under certain conditions of temperature is $Pb_{3x}O_{4x}$, this oxide will have a certain specific gravity. Now if the temperature is increased, the formula might become $Pb_{6x}O_{8x}$, for example, and the oxide will have a different specific gravity. Oxides formed at different temperatures have different specific gravities, and it may be assumed therefore that they have different degrees of polymerization. The acceptance of this theory does not exclude the influence of the crystalline and amorphous modifications upon the specific gravity. The relative degree of polymerization of the two modifications may be such that their specific gravities are about the same.

The amorphous and crystalline modifications of red lead show a marked difference in character when mixed to stiff putty-like paste with water. The paste made from amorphous red lead is tough and plastic, while that made from a crystalline oxide has much less plasticity and shows a tendency to harden and crumble. A commercial red lead made from fused litharge showed lack of plasticity to a marked degree.

We attempted to overcome this lack of plasticity by treating the litharge, before oxidation, with colloids such as tannic acid, glue, etc. One kilogram of the litharge was made to a thin paste with water in which was dissolved one gram of glue or tannic acid. In the treatment of one sample, water without any addition agent was used. These samples were allowed to stand, with frequent stirring and occasional additions of water, for about sixty days, after which they were dried and ground in a mortar to crush the lumps. Portions of about 300 grams of the treated and untreated litharge were then oxidized to red lead. There was no noticeable difference in the plasticity of any of the samples. The only effect that the treatment seemed to have was to cut down the rate of oxidation as noted above, and to make an oxide of a slightly lower specific gravity in the case of the sample treated with water and one of a slightly higher specific gravity where tannic acid and glue were used. In each case the specific gravity of the litharge itself was considerably reduced by the treatment due probably to the formation of lead hydrate.

All of the amorphous samples prepared in the laboratory from white lead showed a high degree of plasticity as did also certain commercial samples which appear under the microscope to be a mixture of amorphous and crystalline oxides. Samples of amorphous oxide, which showed a very high plasticity, were also prepared in the laboratory furnace from metallic lead.

We had no means at hand for making a quantitative study of the plasticity, but the qualitative tests showed such striking differences that we have thought the results worth recording.

The apparent densities which are given in Table I were determined with a Scott volumeter. The values are in grams per cubic inch. The apparent densities of the various samples have no definite relation to the real specific gravities, but vary with the size of the particles. In general, the finer the oxide the lower the apparent density. In the case of an amorphous red lead, however, which was ground for fifty hours in a pebble mill, the apparent density as shown by the Scott apparatus was increased from 18.40 to 24.41. By grinding a crystalline litharge for twenty hours the apparent density was decreased from 36.09 to 28.58, while at the end of fifty hours the apparent density was 29.81. A full discussion of the effect of grinding upon the apparent density will be brought out in a later paper. The sample prepared from atomized lead had the highest apparent density (29.20) of any sample prepared in the laboratory.

[1] Lyndon, "Storage Battery Engineering," pp. 25–26.

Sample B–K–3 was prepared from lead carbonate. The carbonate was made by electrolysis with lead electrodes in a sodium methyl sulphate bath in the presence of sodium carbonate and carbon dioxide. This sample of red lead had an apparent density of 10.34, which is much lower than that of any other oxide which we have examined. The real density was 8.81. Photomicrographs of the carbonate and red lead are shown in Figs. 20 and 21, respectively.

The lead peroxide in all of the samples was determined by distillation with hydrochloric acid, according to the method described by the authors in the Proceedings of the Indiana Academy of Science, 1911.

CONCLUSIONS.

From these experiments we may draw the following conclusions:

1. Red lead may be either crystalline or amorphous.

2. The crystalline modification has no definite form, but the crystals retain the form of the material from which the red lead is made.

3. The specific gravity varies between comparatively wide limits, from 8.32 to 9.16.

4. The variation in specific gravity depends upon: (*a*) the temperature at which the oxide is formed; (*b*) the time of heating; (*c*) the chemical composition; and (*d*) the physical nature of the starting material. It is supposed that these conditions influence the degree of polymerization of the oxide, and that the degree of polymerization is directly responsible for the variation in specific gravity.

5. The apparent density depends mainly upon fineness of the particles of the oxide, decreasing as the fineness increases up to a certain point.

6. The temperature best suited for the formation of red lead varies with the starting material used. About 425° C. to 430° C. is best for white lead, 450° C. to 470° C. for litharge and lead sponge, and about 450° C. for converting lead hydrate and metallic lead to red lead. In fact, 450° C. may be taken as the temperature at which red lead can be economically formed from any suitable starting material.

7. Any red lead is rapidly and completely reduced to litharge at 525° C. to 530° C.

8. Both "yellow" and "red" litharge are roasted to red lead much more slowly after being treated with water, showing that "air separation" of the litharge before roasting is to be preferred to "floating" in water.

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THE CONTINUOUS PURIFICATION OF COAL GAS WITH WEAK AMMONIA LIQUOR.[1]

By J. G. O'NEILL.

In the manufacture of coal gas, the crude gas from the retorts is pulled by an exhauster through a condenser to free it from tar and considerable ammoniacal liquor, and is then forced by the exhauster into another condenser to rid it of excess heat, then through scrubbers which wash out the ammonia, and finally through the purifying boxes where it is purified from hydrogen sulphide and cyanogen, on into the holder. In washing the ammonia from the gas, two scrubbers are used: the first scrubber, taking the gas, washes it with gas liquor, which absorbs a small amount of ammonia and hydrogen sulphide from the gas; the second scrubber washes the gas with fresh water, which completely absorbs the ammonia from the gas.

The present practice of purifying coal gas from hydrogen sulphide and cyanogen consists of passing the gas through a mixture of iron oxide and shavings in air-tight boxes, whereby the hydrogen sulphide and cyanogen in the gas combine with iron oxide to form iron sulphide and ferrocyanides. When the iron oxide no longer takes up any hydrogen sulphide, it is taken from the boxes and exposed to the air, whence by oxidation and throwing off of free sulphur, it again becomes active or "revivified." This operation is repeated four or five times until the percentage of free sulphur in the purifying material increases to about 30 per cent., when the iron oxide will no longer revivify. In earlier times the oxide would revivify and could be used until it contained 60 per cent. free sulphur, but with the modern practice of making gas at much higher temperatures the cyanogen in the gas has greatly increased, and a large percentage of the iron goes to form inactive ferrocyanides. By introducing about 2 per cent. of air into the gas before the purifiers, a certain amount of revivification takes place in the boxes, and reduces the number of times necessary to expose the oxide to the air to again make it active.

There are many disadvantages which we encounter in the iron oxide method of purification, some of which are as follows: the process is non-elastic, consequently the normal increase of gas consumption from year to year; the very much greater consumption during certain periods of the year; the difficulty of obtaining coal low in sulphur—all these conditions are forcing us to rapidly increase our purifying capacity at a very large expense, especially considering the facts that the purifying boxes are extremely bulky and that many coal gas plants are already cramped for space; the danger of a gas explosion every time a box is opened, and the close attention necessary to prevent firing of the oxide when exposed to the air for revivification; the cost of oxide and the labor cost in filling and emptying boxes, also the accumulation of spent oxide, which gradually becomes a nuisance.

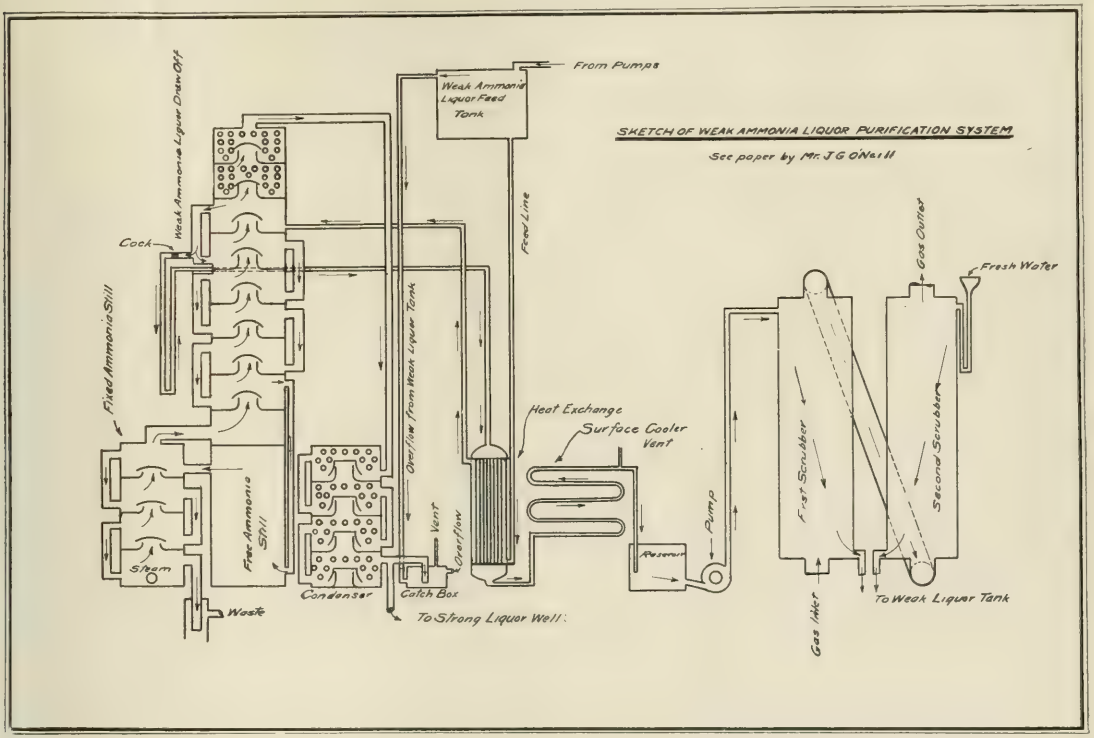
All these disadvantages of oxide purification have been recognized in the past; several investigators have devised other purification processes, none of which have met with general approval. Of these attempts, two are of interest to us, the first by F. C. Hills (British Patent No. 1369, of 1868, and 934, of 1874), whereby he heats ammonia liquor in a special apparatus to 180° F. and obtains a liquor having caustic properties. He washes the unpurified coal gas with this liquor and absorbs the hydrogen sulphide from it. His process failed because of the loss of ammonia in preparing the caustic liquor and because of his failure to determine the correct temperature of the liquor and

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

gas during the washing. Had he determined this correct temperature, he would have found that double the quantity of ammonia from a ton of coal would absorb all the hydrogen sulphide in the gas from a ton of coal, instead of six to seven times the ammonia as is believed to the present time.

Previous papers describing my process will be found in the *Progressive Age* of July, 1911, and August 15, 1911. In this article I wish to lay before you the manner of operation and the results obtained in the use of the process for the past six months.

In my method of operation we absorb the hydrogen



The other process by C. F. Claus (U. S. Patent No. 337,246, of 1886) also sought to use the caustic properties of ammonia. He prepared pure ammonia gas in an elaborate apparatus and introduced the pure ammonia gas directly into the unpurified coal gas, before the scrubbers. This process was fundamentally wrong, it complicated gas purification and increased its cost.

sulphide, cyanogen and some carbon dioxide from the unpurified coal gas by means of a weak alkaline ammonia solution, prepared in an ordinary crude ammonia concentrator. We simply increase the quantity of weak ammonia liquor feeding into the ammonia still and draw off this increase of liquor near the outlet of the first ring, whose contents have been subjected to the action of steam containing a high percentage

	Nov. 11.	Nov. 22.	Dec. 5.	Dec. 7.	Dec. 14.	Jan. 2.
Gas liquor to ammonia still	GPL NH_3—7.00	5.27	4.25	3.87	6.15	7.00
	GPL H_2S—3.20	2.49	1.98	2.31	3.57	3.20
Wash liquor from ammonia still	GPL NH_3—7.48	6.93	5.50	4.79	5.98	8.48
	GPL H_2S—1.46	1.12	.68	.74	.80	1.46
Wash liquor from first scrubber	GPL NH_3—7.48	6.83	5.84	5.03	7.82	9.18
	GPL H_2S—6.12	6.00	3.80	4.43	6.13	8.17
Grains H_2S per 100 cu. ft. in crude gas before scrubbers	807.8	703.8	592.1	703.8	557	966.9
Grains H_2S per 100 cu. ft. in crude gas after scrubbers	276.4	96.3	33.6	44	25	30.6
No. of thousand cu. ft. gas washed per hour	45	40	35	37	45	44
Gallons liquor washed used per hour	720	815	700	900	600	900
Grains H_2S eliminated per gallon liquor wash used	314	298	279	270	399	457

Any advance in the art of gas purification must have for its basis simplicity of operation. It must be more economical of labor, material and of space than the present oxide purification practice, and to be generally adopted it must be applicable to both the large and small coal gas plant. Such a process we have had in operation in our plant for the past six months.

of ammonia vapor. We do not interfere with the actual amount of liquor being distilled or with the operation of the ammonia still. The liquor drawn from this ring is cooled to at least 30° C. and is pumped into the first scrubber, taking the place of the usual gas liquor wash. The only additional apparatus needed to carry out this process is a cooling ap-

paratus which consists of a cooling coil with water spray and a small tubular cooler, which cools the liquor coming from the treatment ring of the ammonia still, thus cooling it for use in the first scrubber. The impurities given off by this liquor in the ammonia still saturate the concentrated ammonia in the condenser of the ammonia still, while the excess impurities pass off into the air after being washed of all traces of ammonia in the catch-pot.

The effects of washing the crude gas with this liquor are shown by the preceding data.

All of the cyanogen in the crude gas is eliminated by the liquor wash.

On an average, we found the liquor wash absorbed from 0.3 to 0.5 per cent. of carbon dioxide from the gas. My opinion is this absorption would be greatly increased with a liquor wash containing a higher percentage of ammonia and with a longer time of contact.

The temperature of the liquor wash to the first scrubber must not be higher than 30° C., neither should the temperature of the gas to the scrubber be higher than 30° C. The best results are obtained when the two temperatures are held at about 25° C. This is the temperature of the gas to the scrubbers that we meet with in ordinary coal gas practice. If gas liquor is substituted for the liquor wash there is practically no increase in hydrogen sulphide in the gas liquor or decrease of hydrogen sulphide in the gas.

Since our scrubbing apparatus was limited to one fresh-water scrubber consisting of eight bell-shaped compartments, I divided the scrubber using the four lower compartments for the liquor wash and the four top ones for fresh water. The results would have been much more satisfactory if we had one scrubber for the liquor wash and one for the fresh water, then we could have used much stronger liquor and would have obtained much higher elimination of impurities per gallon of liquor wash used, without fear of losing any ammonia from insufficient washing.

Another very disagreeable feature of our operation was the uneven make of gas, the amount of gas washed for one hour differing as much as 50 per cent. from another hour of the same day, with little regulation of the liquor wash to meet the increase or decrease in the gas.

Considering all the disadvantages mentioned above, still nowhere in the process was there the least possibility of ammonia loss, also the average yield of ammonia for the six months exceeded the average yield for the six months previous to the installation of the process. No difficulty was experienced in the operation of the ammonia still. The total amount of steam required to operate the ammonia still was not appreciably increased because the cooling water for the ammonia vapors was practically eliminated.

During the month previous to installing the process, 27 per cent. of the coal used for gas-making was a high sulphur coal. The purifying capacity consisted of three boxes, holding a total of 6000 bushels of shavings and iron oxide; during this month we found it impossible to change the oxide in the boxes rapidly enough to purify the gas from hydrogen sulphide, even using new oxide and introducing some air into the gas before the purifiers.

For the six months after installing the liquor purification process, the oxide in the boxes was not changed, no labor was expended on purification, the average monthly output of gas for the first three months increased 12 per cent. and for the last three months decreased 20 per cent. (partly due to coal shortage), the percentage of high sulphur coal used was increased to 50 per cent. of the total, and at the end of this period we found all boxes clean. A very small quantity of air was drawn into the gas before the exhausters, approximately 0.5 per cent.; the quantity of nitrogen in this air introduced into the gas was more than offset by the quantity of carbon dioxide absorbed from the gas by the liquor wash. The gas issuing from the first purifying box in the series would at times show a trace of hydrogen sulphide, but on changing the flow of the gas, so as to remove this box from being first to receive the gas, it would immediately clean up. The gas has gone through the boxes for a month at a time without the gas from the first box showing a trace of hydrogen sulphide with lead acetate paper.

During the severe winter weather, the wash liquor in the pipe line to the scrubber became frozen, consequently for several hours the liquor wash was discontinued. The three boxes went foul even though a short time before they were all perfectly clean. When the wash liquor was again turned on the three boxes gradually cleaned up, proving that by using this liquor wash with a very small quantity of air, the foul boxes could again be made clean, without the necessity of first passing the gas through a clean box.

The actual saving obtained by using this process is very large, even for a small plant, both in labor cost and using high sulphur coal; the process is simpler than oxide purification, elastic, independent of one grade of coal, without danger of fire or explosions, does away with any installation of new purifying boxes, and saves valuable space.

The gas business being a world-wide industry, consequently any improvement in the manufacture of gas is of world-wide interest. With the modern development of uses for gas, any improvement in its manufacture is a direct aid to the progress of the world.

GENEVA, N. Y.

STUDIES ON FISH OILS.[1]

III. Properties of Fish and Vegetable Oil Mixtures.

By GEORGE F. WHITE AND ADRIAN THOMAS.

Received Aug. 14, 1912.

In consequence of the continually increasing interest in the utilization of various fish oils for the most diverse commercial operations, their substitution where possible for the more valuable vegetable oils, and the lack of intimate and complete knowledge of their physical and chemical properties, it has seemed desirable to continue and extend the work which was carried out recently by one of us on fish oils of known origin. The uncertainty of the various tests that have

[1] For previous communications bearing on this subject see THIS JOURNAL, **4**, 106 and 267.

been applied to any oil to detect possible adulteration by another of inferior value has been due rather to the want of a full conception of the behavior of fish oils under all circumstances than to any inherent difficulty connected with the problem. A careful study of mixtures of fish oils with each other and with vegetable oils should yield results of value to both analyst and manufacturer.

In this article there is presented the results of the analysis of dogfish liver (Mustelus canis), soya bean, linseed, china wood oils, and mixtures of these latter with the fish oil. The fish oil was extracted from livers by steam pressure by the method previously described by one of us.[1] Mixtures were made up by weight. The viscosity, density, index of refraction, saponification number, acid number, and iodine number were then measured according to the description given below.

VISCOSITY AND FLUIDITY.

It has been shown that the fluidities of fish oil mixtures are additive, and it should be expected that the same condition would obtain with all oils except in those cases where there is association, decomposition, or some other exceptionally disturbing factor. As the viscosity of an oil is of particular interest to the paint manufacturer, and fish oils are largely used for outside paints or to adulterate oils for other purposes, this property has therefore been especially considered in our study of these oils.

A viscosimeter capable of very accurate measurement gave satisfactory service in our previous work and a new one was made and calibrated according to the method already given. The constants obtained for this instrument are:

Length of capillary (approx.	16 cm.
Volume of left limb	2.1310 cc.
Volume of right limb.....	2.0748 cc.
Pressure correction (30°), left limb	—0.30 cm.
Pressure correction (30°), right limb.....	—0.30 cm.
Ratio of r^4 to l.....	0.00005835
	0.00005822
	0.00005837

The formula used for the calculation of the viscosity was

$$\eta = \frac{\pi r^4 pt}{8vl} - \frac{vd}{8\pi tl},$$

where η is the viscosity, r the radius, and l the length of the capillary, v the volume of liquid passing through the capillary, d the density of the liquid, p the pressure, and t the time of flow. The method of calibration and manipulation has been fully described in previous papers.

In the following tables are presented the results of the viscosity measurements, which were taken at 30°, 50°, 70° and 90°, for the right and left limbs, the average of the two, and the reciprocal of this latter, which is the fluidity. The china wood oil was measured at 35° and the values at 30° extrapolated from the curve, as the oil was so viscous at the lower temperature that the time necessary for a determination was very long. The pure oils were cooled after measurement at 90° and the viscosity redetermined at 30° to note any possible change due to chemical decomposition.

[1] The Soya Bean and China wood oils were furnished us by Marden, Orth, and Hastings, of Boston. The linseed oil was obtained from Eimer & Amend, New York.

TABLE I.—DOGFISH OIL.

Temp.	Viscosity. Right limb.	Left limb.	Average.	Fluidity.
30°	0.4143	0.4140	0.4142	2.414
50°	0.2113	0.2110	0.2112	4.735
70°	0.1247	0.1247	0.1247	8.020
90°	0.08046	0.08063	0.08055	12.41
30°	0.4142	0.4142	0.4142	2.414

TABLE II.—LINSEED OIL.

Temp.	Viscosity. Right limb.	Left limb.	Average.	Fluidity.
30°	0.3312	0.3311	0.3312	3.019
50°	0.1757	0.1757	0.1757	5.692
70°	0.1071	0.1069	0.1070	9.346
90°	0.07103	0.07119	0.07111	14.06
30°	0.3312	0.3316	0.3314	3.017

TABLE III.—SOYA BEAN OIL.

Temp.	Viscosity. Right limb.	Left limb.	Average.	Fluidity.
30°	0.4067	0.4058	0.4063	2.461
50°	0.2060	0.2065	0.2063	4.847
70°	0.1207	0.1209	0.1208	8.278
90°	0.07807	0.07836	0.07822	12.79
30°	0.4069	0.4067	0.4068	2.458

TABLE IV.—CHINA WOOD OIL.

Temp.	Viscosity. Right limb.	Left limb.	Average.	Fluidity.
30°	. .	. . .	1.859	0.5379
35°	1.591	1.587	1.589	0.6293
50°	0.7796	0.7805	0.7801	1.282
70°	0.3699	0.3717	0.3708	.2.697
90°	0.2126	0.2128	0.2127	4.702
35°	1.933	1.957	1.946	0.5139

TABLE V.—DOGFISH LIVER—LINSEED OIL MIXTURES.

Temp.	Right limb.	Left limb.	Average.	Fluidity.
25 Per cent. Linseed. Viscosity.				
30°	0.3954	0.3943	0.3949	2.533
50°	0.2027	0.2018	0.2023	4.943
70°	0.1204	0.1201	0.1203	8.313
90°	0.07784	0.07798	0.07791	12.84
50 Per cent. Linseed.				
30°	0.3712	0.3712	0.3712	2.694
50°	0.1930	0.1925	0.1928	4.943
70°	0.1150	0.1151	0.1151	8.688
90°	0.07554	0.07561	0.07558	12.23
75 Per cent. Linseed.				
30°	0.3555	0.3556	0.3556	2.812
50°	0.1866	0.1866	0.1866	5.354
70°	0.1123	0.1124	0.1124	8.897
90°	0.07425	0.07427	0.07426	13.47

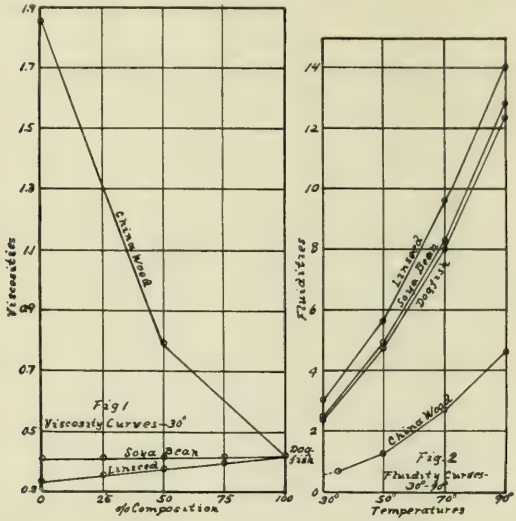
TABLE VI.—DOGFISH LIVER—SOYA BEAN OIL MIXTURES.

Temp.	Right limb.	Left limb.	Average.	Fluidity.
25 Per cent. Soya Bean.				
30°	0.4121	0.4125	0.4123	2.425
50°	0.2121	0.2094	0.2108	4.744
70°	0.1234	0.1227	0.1231	8.123
90°	0.07952	0.07934	0.07941	125.9
50 Per cent. Soya Bean.				
30°	0.4099	0.4130	0.4115	2.430
50°	0.2074	0.2082	0.2078	4.813
70°	0.1215	0.1227	0.1221	8.190
90°	0.7930	0.07954	0.07942	12.59
75 Per cent. Soya Bean.				
30°	0.4074	0.4071	0.4073	2.455
50°	0.2072	0.2075	0.2074	4.822
70°	0.1210	0.1214	0.1212	8.251
90°	0.07852	0.07865	0.07859	13.72

TABLE VII.—DOGFISH LIVER—CHINA WOOD OIL MIXTURES.
50 Per cent. China Wood Oil.
Viscosity.

Temp.	Right limb.	Left Limb.	Average.	Fluidity.
30°	....	....	0.7950	1.258
35°	0.6926	0.6942	0.6934	1.442
50°	0.3895	0.3875	0.3885	2.574
70°	0.2085	0.2080	0.2083	4.801
90°	0.1258	0.1259	0.1259	7.943

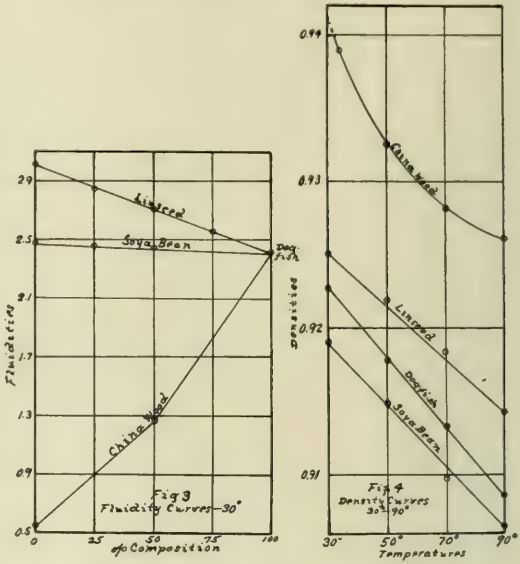
The viscosity and fluidity are pictured graphically in Figs. 1–3. According to Bingham's fluidity hypothesis,[1] the fluidities of liquid mixtures should be



additive when there is no association or action between the components. This is true when the fluidity-temperature curve is linear. It may be seen from Fig. 2 that the fluidities of the dogfish, linseed and soya bean oils are nearly linear functions of the temperature and their curves have the same slope.

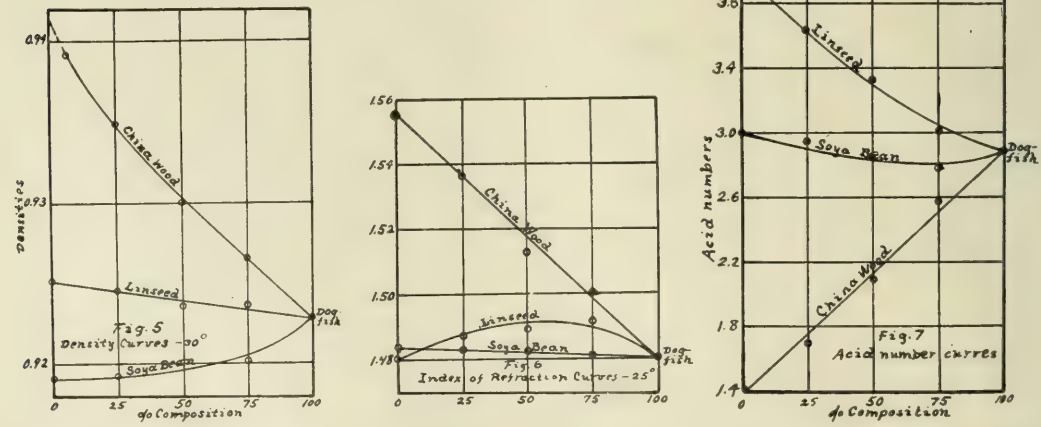
Fig. 3 shows that mixtures of these oils have fluidities which are linear functions of the composition. On the other hand, china wood oil behaves differently. Its fluidity curve does not have the same slope as that of the other oils, and also its fish oil mixtures do not give additive fluidities. The data in Table IV shows that it changes in composition on being heated to 90° since its viscosity at 35° increases from 1.589 to 1.946. The values for the other oils remain constant.

It is interesting to note how much more viscous



the china wood oil is than the other three oils, this property being a good test of its purity, since a little adulteration by other oils of viscosity approximating the others would lower the viscosity of the china wood oil markedly.

The viscosity curves of the mixtures are given for 30° in Fig. 1. As has been shown before, the linear



curves obtained for the soya bean and linseed oil mixtures were to be expected since the viscosities of the components are nearly identical. Neither the

[1] *Z. physik. Chem.*, **1909**, 1.

viscosity nor fluidity curves for the china wood oil mixtures are linear.

DENSITY.

There is little to be said in regard to the data furnished by specific gravity determinations. These were made by use of the Ostwald pycnometer. The results are given in Table VIII and shown by graphs in Figs. 4–5. Fig. 4 shows that the density is a linear function of the temperature over the range at which we worked, except with the china wood oil, the composition of which changes on heating. Linseed and dogfish liver oil mixtures have additive densities at 30° while the other mixtures do not. These data were of value to us, principally in our calculation of the viscosities.

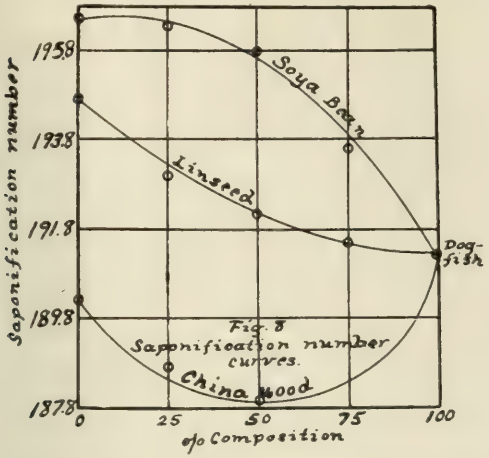


Fig. 8
Saponification number curves.

TABLE VIII.—DENSITIES OF OILS.

	30°.	35°.	50°.	70°.	90°.
Dogfish liver	0.9228	....	0.9175	0.9131	0.9082
Linseed	0.9251		0.9219	0.9183	0.9141
Soya bean	0.9191	....	0.9149	0.9095	0.9063
China wood	0.9411	0.9389	0.9324	0.9279	0.9260
Dogfish liver–25 per cent. linseed	0.9237		0.9158	0.9120	0.9090
Dogfish liver–50 per cent. linseed	0.9235	....	0.9124	0.9051	0.8986
Dogfish liver–75 per cent. linseed	0.9245	....	0.9169	0.9100	0.9051
Dogfish liver–25 per cent. soya bean	0.9200	....	0.9158	0.9111	0.9082
Dogfish liver–50 per cent. soya bean	0.9200	....	0.9149	0.9076	0.9055
Dogfish liver–75 per cent. soya bean	0.9191	....	0.9141	0.9076	0.9046
Dogfish liver–25 per cent. china wood	0.9268	0.9237	0.9149	0.9103	0.9074
Dogfish liver–50 per cent. china wood	0.9300	0.9289	0.9255	0.9209	0.9188
Dogfish liver–75 per cent. china wood	0.9348	0.9322	0.9245	0.9230	0.9204

INDEX OF REFRACTION.

The refractive indices were measured by the use of a microscope, the apparent and true depths of a column of liquid being compared. Fig. 6 shows that the index of refraction is not a good criterion of the composition of linseed and soya bean oils when being tested for the presence of fish oil, but it should be valuable in the case of china wood oil, the refractive index of which is considerably greater than that of the other oils. This has been brought out by

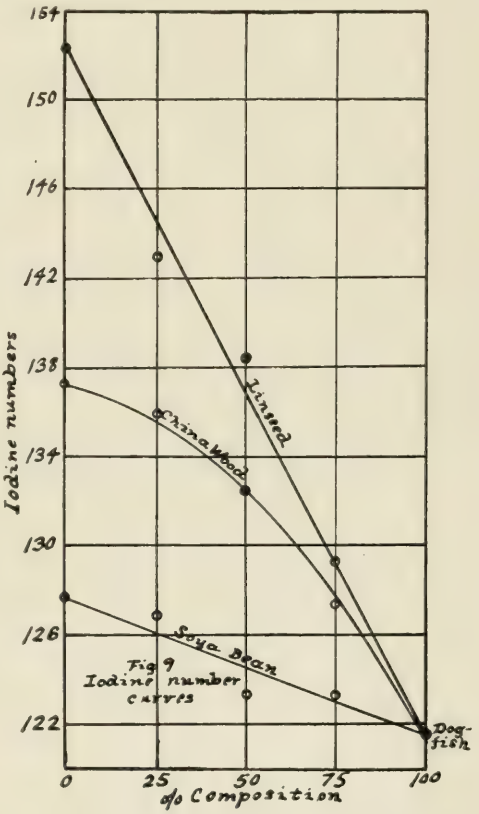


Fig. 9
Iodine number curves

TABLE IX.

Oil	Index of refraction at 25°.	Acid number. 1.	2.	Av.	Saponification number. 1.	2.	Av.	Iodine number. 1.	2.	Av.
Dogfish	1.4801	2.91	2.94	2.93	191.3	191.2	191.3	122.7	120.3	121.5
Linseed	1.4805	3.98	4.01	4.00	194.0	195.3	194.7	152.1	152.7	152.4
Soya bean	1.4837	3.08	3.08	3.08	196.7	196.4	196.5	130.5	125.1	127.8
China wood	1.5560	1.47	1.49	1.48	190.1	190.2	190.2	(124.4?)	137.1	137.1
Dogfish–25 per cent. linseed	1.4948	3.06	3.06	3.06	191.4	191.6	191.5	129.2		129.2
50 per cent. linseed	1.4872	3.41	3.43	3.42	192.0	192.4	192.2	137.9	139.1	138.5
75 per cent. linseed	1.4870	3.75	3.68	3.72	191.0	194.9	193.0	144.3	145.1	144.7
25 per cent. soya bean	1.4790	2.85	2.85	2.85	193.5	193.5	193.5	123.3	123.1	123.2
50 per cent. soya bean	1.4819	2.94	2.92	2.93	195.6	195.9	195.8	123.1	122.1	122.6
75 per cent. soya bean	1.4834	3.00	3.03	3.02	196.4	196.1	196.3	126.9	127.7	127.3
25 per cent. china wood	1.4997	2.60	2.72	2.66	193.2	193.0	193.1	128.0	126.4	127.2
50 per cent. china wood	1.5120	2.14	2.19	2.17	187.6	187.9	187.8	133.2	131.4	132.3
75 per cent. china wood	1.5363	1.78	1.76	1.77	188.5	188.9	188.7	135.6	136.5	136.1

the work of Wise[1] in a recent study of this oil.

ACID, SAPONIFICATION, AND IODINE NUMBERS.

The results of the measurements of the acid, saponification and iodine numbers are presented in Table IX and Figs. 7–9. The first two numbers represent the milligrams of potassium hydroxide necessary for one gram of oil, while the iodine numbers were obtained by Hübl's method, being per cent. iodine absorbed by the oil.

The acid numbers are seen to be generally additive for the mixtures, while the saponification numbers offer no general behavior. The iodine numbers are additive for the linseed and soya bean mixtures, the china wood mixtures, however, giving a hyperbolic curve. As the iodine number of the linseed is so much higher than that of the dogfish liver oil, this, as is well known, furnishes good evidence of the purity of the former. The numbers for the other vegetable oils are so near those of the fish oil that great value cannot be placed in these tests. Reference may be made to the work of McIlhiney[2] for a method of examining china wood oil.

SUMMARY.

1. The fluidities of fish and vegetable oil mixtures are additive, except where there is decomposition of either component on heating.

2. The viscosities of these mixtures are also additive when the values for the components approximate each other closely.

3. The fluidities of vegetable oils are nearly linear functions of the temperature. It has been previously shown that this holds true for various fish oils.

4. The fluidity of china wood oil, as it is unusually low, is a good test of its purity.

5. The specific gravities of the mixtures are approximately additive and vary linearly with the temperature. The density of china wood oil is very high.

6. The index of refraction, acid number, and saponification number of the mixtures do not allow any general conclusions. The acid number of linseed oil is high, and that of china wood oil low, compared with that of dogfish liver oil. The refractive index of china wood oil is lowered by the introduction of small amounts of fish oil.

7. The low iodine number of the dogfish liver oil makes the presence of this oil in vegetable oils known by marked lowering of their iodine values.

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THE RELATION OF THE REFRACTIVE INDEX OF SODA-BARIUM AND SODA-LIME GLASSES TO THEIR CHEMICAL COMPOSITION.

By EDWIN WARD TILLOTSON, JR.

Received July 1, 1912.

Many attempts have been made to discover the relation which exists between the refractive index and the chemical composition of substances, and many formulae have been derived to express this relation.

[1] THIS JOURNAL, **4**, 497 (1912).
[2] *Ibid.*, **4**, 496 (1912).

Nearly all of these expressions are based upon a constant known as the specific refractive power which has been defined by Gladstone and Dale[1] as

$$\frac{n - 1}{d} = K$$

and by Lorentz[2] and Lorenz[3] as

$$\frac{n^2 - 1}{n^2 + 2} \times \frac{1}{d} = K'.$$

This specific refractive power (K and K′) represents a relation between the refractive index and the density of a substance and is nearly, but not quite, constant over a large range of temperature. It is also dependent on both the chemical composition and the constitution, or structure, of the compound. The product of the specific refractive power and the molecular weight is known as the molecular refractive power and has been found, for many organic compounds, to be the sum of its several atomic refractive powers modified by the structure or atomic arrangement within the molecule.

These relationships have been studied to only a limited extent in connection with silicates. Owing to our lack of knowledge of the compounds which are formed in a glass or of their atomic structure, the derivation of atomic refractive powers for the glass forming oxides is impossible. Investigations have, therefore, been limited to the study of mixtures of pure silicates. Larsen[4] has shown that the specific refractive power of mixtures of calcium and magnesium silicate is a nearly linear function of the composition, calculated in percentages by weight, and the writer has shown[5] that this is also true, within limits, of soda-lime glasses.

Neither the refractive index nor the specific refractive power of mixtures is necessarily a linear function of the composition. In addition to the changes in volume which may occur on mixing two liquids, there may be a similar change in the specific refractive power which may or may not be parallel with, or proportional to, the change in volume. Schütt[6] and Pulfrich[7] have derived some rather complex formulae to express these relations, both of which show excellent agreement with the experimental data. Schütt's formula is as follows,

$$K = \frac{\Sigma k}{1 - c\,(a + bp)},$$

in which K is the specific refractive power of the mixture, Σk is the sum of the specific refractive powers of the components calculated by percentages by volume, c is the percentage change in volume on mixing, and $(a + bp)$ is a factor dependent on a similar change in the specific refractive power. Pulfrich's formula is analogous to the above and is as follows,

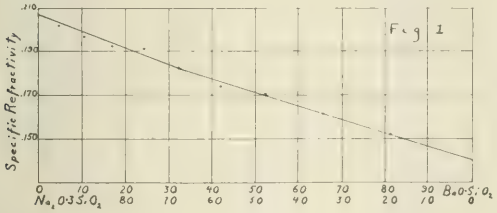
$$K\left(\frac{1 - ac}{1 - c}\right) = \Sigma k,$$

[1] *Phil. Trans.*, **337** (1863).
[2] *Wied. Ann.*, **9**, 641 (1880).
[3] *Ibid.*, **11**, 70 (1880).
[4] *Am. J. Sci.*, **28**, 263 (1909).
[5] THIS JOURNAL, **4**, 246 (1912).
[6] *Z. phys. Chem.*, **9**, 349 (1892).
[7] *Ibid.*, **4**, 561 (1889).

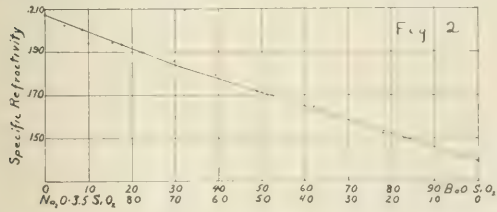
in which K, Σk and c have the same significance as before and a is a factor dependent on the change in the specific refractive power. In applying either of these formulae to isomorphous mixtures, or to mixtures which do not change in volume on mixing, the factor c becomes zero, and both formulae reduce to $K = \Sigma k$. Mixtures of silicates closely approach this condition. The densities of glasses, differing widely in composition, are very nearly the same as those calculated[1] from their components. We should, therefore, expect the specific powers of mixtures of silicates to be a very nearly linear function of their compositions, expressed in percentages by volume.

This paper is a partial account of an investigation on the refractive index and specific refractive power of some soda-barium glasses for the purpose of throwing light on the relation between refractive index and composition and possibly to identify compounds or double silicates which may exist. The preparation of the glass, the procedure adopted for carrying out these experiments, and the probable errors have been described in a previous paper.[2] The Gladstone and Dale formula for the specific refractive power has been employed throughout on account of its simplicity and ease of manipulation, and also because a large number of comparisons in this work have not disclosed any appreciable superiority of one formula over the other. The compositions of the glasses have been calculated as percentages by volume in accordance with the formula of Schütt and Pulfrich given above.

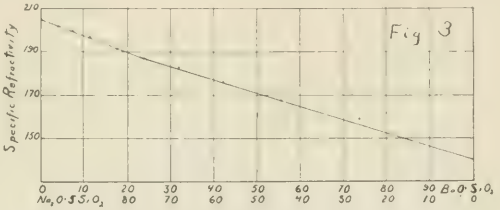
The results obtained with soda-barium glasses are shown graphically in Figs. 1–4, in which the composition of the glasses is represented by the abscissas and



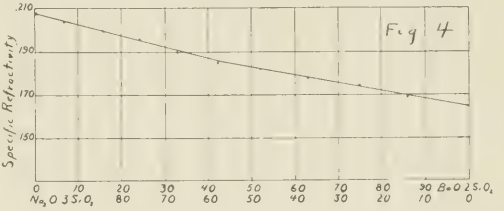
the specific refractive powers by the ordinates. The glasses, whose specific refractive powers are shown in Fig 1, varied in composition from $Na_2O.3SiO_2$ to $BaO.SiO_2$, those in Fig. 2 from $Na_2O.3.5SiO_2$ to $BaO.SiO_2$, those in Fig. 3 from $Na_2O.5SiO_2$ to



$BaO.SiO_2$, and those in Fig. 4 from $Na_2O.3SiO_2$ to $BaO.2SiO_2$. Fig. 4 is instructive in that it shows distinctly two straight lines meeting at a point corresponding to a composition consisting of equimolecular proportions of Na_2O and BaO—in this case Na_2O.

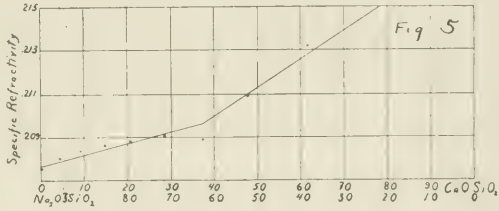


$BaO.5SiO_2$. This second line is also observable in the other figures, but is not so distinct because of the lack of data for glasses approaching barium metasilicate in composition. These glasses possess a very high melting point, crystallize readily and are subject



to large experimental errors both in the composition and in the measurement of the refractive index. The data is sufficient, however, to indicate the direction of the two lines. If the conclusion that the specific refractive powers are additive is true, this change in direction of the curve indicates a compound at the point where the break occurs, which in this case is of the type $Na_2O.BaO.xSiO_2$.

In Fig. 5 are shown, for comparison, the specific



refractive powers of the soda-lime glasses, which were described in a former paper, recalculated and plotted in terms of percentages by volume. The results are, in general, the same as those previously found, and show plainly the two lines meeting at a composition corresponding to $2Na_2O.3CaO.9SiO_2$.

In Tables I to V are presented the numerical data corresponding to Figs. 1–5, respectively. The first four columns in these tables show the composition of the glasses in molecular per cent. and in percentages by volume. In the fifth column are given the densities as calculated from the composition;[1] in the sixth, the observed refractive index for white light; and in the seventh the values of K, calculated, with the aid of Gladstone and Dale's formula, from the data in columns five and six.

[1] Winkelmann and Schott, *Ann. d. Phys. und Chem.*, **51**, 697 (1894). Tillotson, THIS JOURNAL, **3**, 897 (1911).

[2] Tillotson, *Loc. cit.*

[1] Tillotson, *Loc. cit.*

TABLE I.

$BaSiO_3$. Mol. per cent.	SiO_2. Vol. per cent.	BaO. Vol. per cent.	Na_2O. Vol. per cent.	D calc.	N obs.	K obs.	K calc.	N calc.	N calc.-obs.
0	78.1	....	21.9	2.41	1.500	0.20747	0.2075	1.5000	±0.0000
10	76.6	2.3	21.0	2.515	1.510	0.2025	0.2038	1.5126	+0.0026
20	75.6	4.9	19.5	2.625	1.525	0.1999	0.1992	1.5229	—0.0021
30	74.0	7.8	18.2	2.755	1.530	0.1925	0.1946	1.5361	+0.0061
50	70.6	14.7	14.7	3.055	1.560	0.1835	0.1830	1.5591	—0.0009
60	68.4	18.9	12.7	3.25	1.572	0.1760	0.1769	1.5749	+0.0029
70	65.9	23.9	10.2	3.48	1.593	0.1705	0.1702	1.5923	—0.0007
80	62.8	29.8	7.4	3.74	1.606	0.1620	0.1619	1.6055	—0.0005
90	59.2	36.9	3.9	4.05	1.648	0.1520	0.1521	1.6160	+0.0012

TABLE II.

$BaSiO_3$. Mol. per cent.	SiO_2. Vol. per cent.	BaO. Vol. per cent.	Na_2O. Vol. per cent.	D calc.	N obs.	K obs.	K calc.	N calc.	N calc.-obs.
0	80.6	....	19.4	2.40	1.495	0.2062	0.2066	1.4958	+0.0008
10	79.7	2.0	18.3	2.49	1.503	0.2020	0.2031	1.5057	+0.0027
20	78.3	3.8	17.9	2.57	1.515	0.2005	0.2001	1.5142	—0.0008
30	76.7	7.0	16.3	2.71	1.5255	0.1939	0.1950	1.5284	+0.0029
33⅓	76.0	8.0	16.0	2.76	1.533	0.1931	0.1932	1.5332	+0.0002
40	74.8	10.0	15.2	2.845	1.540	0.1898	0.1901	1.5408	+0.0008
50	72.7	13.5	13.8	3.01	1.560	0.1860	0.1843	1.5547	—0.0053
60	70.5	17.8	11.7	3.20	1.575	0.1797	0.1782	1.5702	—0.0048
70	67.7	22.5	9.8	3.41	1.585	0.17156	0.1720	1.5865	+0.0015
80	64.3	28.5	7.2	3.675	1.604	0.16435	0.1638	1.6019	—0.0021
90	60.0	36.3	3.7	4.03	1.613	0.1520	0.1538	1.6198	+0.0068

TABLE III.

$BaSiO_3$. Mol. per cent.	SiO_2. Vol. per cent.	BaO. Vol. per cent.	Na_2O. Vol. per cent.	D calc.	N obs.	K obs.	K calc.	N calc.	N calc.-obs.
10	84.3	1.8	13.9	2.45	1.496	0.2024	0.2019	1.4947	—0.0013
20	83.3	3.4	13.3	2.52	1.504	0.2000	0.1992	1.502	—0.0020
30	82.0	5.2	12.8	2.605	1.515	0.1973	0.1964	1.5126	—0.0024
40	80.1	8.0	11.9	2.74	1.526	0.19196	0.1920	1.5261	+0.0001
50	78.0	10.9	11.1	2.865	1.537	0.18776	0.1871	1.5360	—0.0010
60	75.5	14.5	10.0	3.03	1.555	0.18316	0.1823	1.5524	—0.0027
70	72.3	19.2	8.5	3.245	1.571	0.1761	0.1760	1.5711	+0.0001
80	68.3	25.3	6.4	3.52	1.590	0.1676	0.1675	1.5899	—0.0001
90	62.6	33.6	3.8	3.90	1.622	0.1595	0.1562	1.6091	+0.0016

TABLE IV.

$BaSiO_3$. Mol. per cent.	SiO_2. Vol. per cent.	BaO. Vol. per cent.	Na_2O. Vol. per cent.	D calc.	N obs.	K obs.	K calc.	N calc.	N calc.-obs.
10	77.8	2.0	20.2	2.495	1.508	0.2035	0.2038	1.5085	+0.0005
20	76.8	4.7	18.5	2.615	1.520	0.1989	0.1993	1.5211	+0.0010
30	76.4	7.1	16.5	2.72	1.531	0.1955	0.1950	1.5304	—0.0006
40	75.7	9.7	14.6	2.83	1.537	0.1898	0.1903	1.5385	+0.0015
50	74.8	12.5	12.7	2.95	1.5475	0.1855	0.1853	1.5466	—0.0009
60	74.1	15.4	10.5	3.075	1.5594	0.1820	0.1816	1.5584	—0.0010
70	72.9	19.0	8.1	3.21	1.5718	0.1780	0.1780	1.5718	+0.0000
80	72.4	22.1	5.5	3.37	1.5847	0.1735	0.1738	1.5857	+0.0010
90	71.7	25.4	2.9	3.51	1.5945	0.1693	0.1700	1.5967	+0.0022
100	70.8	29.2	....	3.675	1.6054	0.1648	0.1650	1.6063	+0.0009

TABLE V.

$CaSiO_3$. Mol. per cent.	SiO_2. Vol. per cent.	CaO. Vol. per cent.	Na_2O. Vol. per cent.	D calc.	N obs.	K obs.	K calc.	N calc.	N calc.-obs.
10	77.8	1.5	20.7	2.43	1.5064	0.2085	0.2080	1.5054	—0.0010
20	77.2	3.1	19.7	2.455	1.5115	0.2084	0.2080	1.5106	—0.0009
30	76.4	5.0	18.6	2.48	1.5172	0.2085	0.2085	1.5172	±0.0000
40	75.7	7.2	17.1	2.51	1.5240	0.2088	0.2087	1.5238	—0.0002
50	74.8	9.7	15.5	2.55	1.5334	0.2092	0.2090	1.5330	—0.0004
50	74.8	9.7	15.5	2.55	1.5300	0.2087	0.2090	1.5330	+0.0030
60	73.6	12.8	13.6	2.60	1.5425	0.20866	0.2090	1.5433	+0.0008
70	72.3	16.4	11.3	2.65	1.5590	0.21094	0.2107	1.5584	—0.0006
80	70.6	21.1	8.3	2.72	1.5796	0.21310	0.2129	1.5791	—0.0005
80	70.6	21.1	8.3	2.72	1.5800	0.21323	0.2129	1.5791	—0.0009

Since the specific refractive power is additive for glasses of certain well defined compositions, it is possible to calculate the specific refractive powers which the several oxides show in those glasses. They are as follows:

SiO_2	0.1995
BaO	0.0500
CaO	0.2410
Na_2O	0.2360

These empirical factors apply for glasses varying in composition from the pure sodium silicates up to the point where the change in direction of the specific refractive power curve takes place and includes nearly all of the typical commercial glasses. The specific refractive powers and the refractive index of these glasses have been computed by the use of these factors, and are given in columns eight and nine in the tables. The specific refractive powers of the glasses which occur between the break in the curve and the

pure barium and calcium silicates were not calculated from factors, but were taken from the curves in Figs. 1–4. It is possible to derive factors which satisfy conditions for these glasses, but they are quite different from the factors given above and are unsatisfactory for calculating the specific refractive power for glasses of this composition. Not only is the factor for every oxide different from those in the above table, but the same oxide may possess different refractive powers in different glasses of this type. For example, SiO_2 possesses a different specific refractive power in soda barium glasses from what it does in soda lime glasses and a different value in $BaO.SiO_2$ from what it does in $BaO.2SiO_2$. This behavior is doubtless to be explained as due to the compounds which are present, and if so, will prove a valuable aid in determining the true constitution of a glass. To illustrate this point, the glass in Table IV, containing 90 molecular per cent. of $BaO.2SiO_2$, has the following composition:

	Per cent.
$Na_2O.BaO.4SiO_2$	19.5
$BaO.2SiO_2$	76.4
SiO_2	4.1

The specific refractive power of $Na_2O.BaO.4SiO_2$, calculated from the factors given above, is 0.1830, that of $BaO.2SiO_2$ experimentally found is 0.1650, and that of SiO_2 is 0.1995. Using these factors, the specific refractive power of a glass of the above composition is 0.1700—a value which is in fair agreement with that found experimentally (0.1693) but which is not in harmony with the value calculated from a consideration of the oxides alone.

SUMMARY.

1. Several series of soda-barium and soda-lime glasses have been made and their refractive indices measured.

2. The existence of compounds of the types Na_2O, $BaO.xSiO_2$ and $2Na_2O.3CaO.xSiO_2$ have been indicated.

3. The specific refractivities of these glasses computed with the aid of the calculated densities are additive from the pure sodium silicate up to the double silicate and from the double silicate to the barium or calcium silicate.

4. Factors have been derived by which the specific refractive power of soda-lime and soda-barium glasses may be calculated within the limits described above from the percentages by volume of the oxides. These are, for use with Gladstone and Dale's formula, as follows:

SiO_2	0.1995
BaO	0.0500
CaO	0.2410
Na_2O	0.2360

5. Since these factors have values which are characteristic of the compounds which may be present, an exact knowledge of these compounds is necessary for a thorough understanding of the optical behavior of a glass.

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COMPOSITION OF THE SALINES OF THE UNITED STATES.

II. Natural (Subterranean) Brines and Mother Liquors from Natural Brines.

By J. W. TURRENTINE, with analyses by A. R. MERZ AND R. F. GARDNER.

Received Aug. 7, 1912.

The term natural brine has been restricted in these papers to mean the salt solution of various degrees of salinity which occur in more or less deep lying strata, as contrasted with those which are found on the surface, in saline creeks, lakes or marshes, or just beneath the surface of saline flats. This definition is justified when it is remembered that these brines constitute an important source of salt in a number of states east of the Rocky Mountains and their employment in the manufacture of salt in this country antedates that of rock salt. This classification also differentiates them from these other brines, prepared by dissolving rock salt, used extensively in the manufacture of salt, which have been discussed in the foregoing chapter.

Natural brines are confined to no geological horizon. Their occurrence seems to be correlated with porosity more than with any other property of their containing strata.

Distribution.—In Pennsylvania, Ohio, West Virginia and Michigan, salt is manufactured on a commercial scale from natural brines. However, their distribution is by no means confined to the rocks underlying these states, but is found in other states, associated especially with petroleum and natural gas. This association, it appears probable, is attributable only to the fact that these three mobile products seek the natural reservoirs afforded by the more porous strata.

The salt industries of Southeastern Ohio in Meigs and Morgan Counties derive their brines from certain previous strata underlying the Conemaugh formation.[1] These strata occur at different horizons. As the brines have been exhausted in the upper strata, at a depth of 300 feet, the wells have been deepened until now they have attained a depth of about 1600 feet.

In West Virginia salt is made from natural brines in the Ohio and Kanawha Valleys. The former region, Mason County, lies closely adjacent to the Pomeroy region of Ohio, and the brines there obtained come from the same strata as do those obtained at Pomeroy. In the Kanawha Valley the wells penetrate the saliferous sandstones of the Pottsville series of the Carboniferous,[2] which lie at a depth of 600 to 1000 feet below the surface. In Michigan they are derived from the Marshall sandstones which, in the Saginaw region, lie at a depth of about 1000 feet below the surface.

Origin.—Theoretically, natural brines are actual occlusions of sea water, bottled up, so to speak, within the porous strata which now contain them by so-called impervious strata; because of their isolation they have remained unaltered since their occlusion and, therefore, are representative of the sea which was instrumental in the formation of their enclosing rocks.

[1] Bownocker, Geol. Survey Ohio, *Bull.* 8.

[2] Harris, Geol. Survey Louisiana, *Bull.* 7.

Presuming for the moment that the natural brines are occlusions of sea water, from their chemical composition it is evident that the sea of which they are a remnant was of a quite different composition from the ocean of the present age, or from the sea from which the Stassfurt deposits were crystallized—the sea of an earlier geological age, and from the present inland seas. Natural brines differ most markedly from ocean water in the ratio between calcium and sulfate ions. In ocean water that ratio is small, while in natural brines it is large.

Certain physico-chemical and geo-chemical considerations make it appear that natural brines should be regarded as the product of the leaching of beds of rock salt, or, less probably, of great masses of rocks which have been laid down in brine, rather than occlusions of sea water.

It cannot be said from existing data what the composition of seepage water would be on emerging from a bed of rock salt. Probably it would be a saturated solution of sodium chloride and, perhaps, of calcium sulfate, since these are the two solids present in largest amounts. Its content in these two constituents would be determined by their solubility in that solution, or mutual solubility. Beyond that concentration, of course, no more of them could be dissolved whatever the actual or relative amount in which they were present in the beds of salt. In addition, the other soluble impurities present in the rock salt would be found in the seepage water. Their ultimate origin would be the mother liquor from the sodium chloride crystallization. Their concentration would be determined by several factors, among which may be mentioned the amount in which they were present in the rock salt and the thickness of the strata penetrated by the seepage water. Their concentration in the seepage water would be limited ultimately by their solubility in that solution and not by the relative amounts in which they were present. In other words, the seepage water from a salt bed may not be at all representative in composition of the rock salt which it has penetrated. Qualitatively, the seepage water might be expected to contain the same salts that were found in the sea from which the rock salt was crystallized, since the impurities in the rock salt had their origin in this sea water. That the natural brines are so markedly different from any lake or sea water with which we are acquainted is at first sight a strong indication of the erroneousness of our theory.

At least two factors are operative in the occlusion of other saline substances which take place in the crystallization of sodium chloride from an impure brine—namely, *mechanical occlusion* of droplets of mother liquor and *adsorption*. Impurities occluded in the former way are present in the form in which they occur in the mother liquor; those in the latter way may be entirely different. Since adsorption is a selective phenomenon, from a solution of sodium chloride and calcium sulphate, calcium ions may have been adsorbed in proportionately larger amounts than sodium ions, and chloride than sulfate ions. In the subsequent leaching of the precipitates by a solution of a lower concentration than that in which the precipitates were deposited, the adsorbed ions, in part, may have been forced back into solution. A solution would have resulted, then, in which the ratios between the ions had been determined by the coefficients of adsorption of the ions in the respective solutions.

It is proposed that in some such way the natural brines were produced—by the permeation of strata or rock salt or shales containing adsorbed saline materials, by seepage waters. Their high concentration in sodium chloride strongly suggests that they have passed through rock salt rather than through shales. The presence of potassium salts in them further suggests the same conclusion. In this way the presence in natural brines of any or all of the saline substances found therein may be accounted for, and thus may be explained the excess of calcium over sulfate ions.

Technology.—The technology of the natural brines is essentially the same as that of the artificial brines. However, since the mother liquors in many instances are to be utilized for the recovery of calcium chloride, the preliminary precipitation is restricted to the treatment for the elimination of suspended solids, hydrogen sulphide and iron.

The method of obtaining natural brines from the earth is much the same as that employed in obtaining petroleum. A hole is drilled to the saliferous strata, a cavity for the accumulation of the brine is made by "shooting" with nitroglycerine and the brine is then pumped.

For the recovery of calcium and magnesium chlorides the mother liquors from the evaporators are further evaporated to the point where, on cooling, the ultimate possible crystallization of sodium chloride is accomplished. The mother liquor from this crystallization is evaporated in kettles, heated with steam coils, to the concentration at which on cooling the mass solidifies. The water present is taken up as water of crystallization. The product is a mixture of hydrated calcium and magnesium chlorides, with the calcium salt in preponderating amount.

For the recovery of bromine, the mother liquor, before the final evaporation, is acidified and is subjected to distillation in the presence of a suitable oxidizing agent, such as a chlorate. The acid is neutralized subsequently with lime and the solution is then evaporated for the preparation of the solid calcium chloride.

The origin of the samples and the methods of analysis employed have been mentioned in the discussion of the composition of artificial brines, in a former chapter and need not here be repeated.

HISTORICAL.

Numerous analyses of natural brines of Michigan and of salt prepared from them are reported by Rominger.[1] Eckel[2] has compiled a table of analyses of both natural and artificial brines from various American and foreign sources, which are quoted by Harris.[3]

[1] Geol. Survey Michigan, Vol. III, appen. B, pp. 179–196.
[2] U. S. Geol. Survey, *Bull.* **213,** 415 (1902).
[3] Geol. Survey, Louisiana, *Bull.* **7,** 84 (1907).

ANALYTICAL RESULTS.

TABLE I.—NATURAL BRINES OF MICHIGAN.

B. of S. No.	72.	73.	74.	75.	76.	77.	78.	79.	80.	81.
Serial No.	64.	66.	68.	71.	73.	76.	79.	83.	84.	88.
K	trace	0.4	1.4	0.8	1.0	trace	1.2	trace	trace	0.8
Na	77.8	100.0	129.7	78.2	86.6	69.3	52.5	85.5	111.5	132.6
Ca	10.8	7.6	12.8	10.8	16.0	36.6	50.2	15.8	4.2	2.8
Mg	3.8	1.0	3.6	3.2	4.4	8.6	11.6	4.0	13.2	0.4
Cl	145.4	155.1	155.4	145.9	172.8	196.4	205.4	163.0	205.4	205.4
SO_4	4.2	2.4	26.0	2.2	1.2	1.2	0.6	0.6	1.8	3.6
Br	0.4	1.7	2.0	0.5	0.4	2.2	trace	2.0	2.8	1.1
Conventional Combinations.										
KCl	trace	0.8	2.7	1.6	1.9	trace	2.3	trace	trace	1.5
NaCl	197.3	239.6	242.8	198.4	219.7	175.8	133.3	217.0	283.2	334.0
$CaCl_2$	24.9	18.3	35.4	27.4	42.9	99.8	183.0	42.9	9.4	3.6
$MgCl_2$	13.3	3.9	6.3	9.8	15.3	32.5	45.5	5.5	37.2	1.6
Na_2SO_4	...	...	39.7	...	...	...	...	...	...	...
$CaSO_4$	6.0	3.4	trace	3.1	1.7	1.7	0.9	0.9	2.6	5.1
$MgBr_2$	0.8	...	4.0	1.2	0.9	2.7	7.8	4.6	6.5	1.4
							$FeCl_3$			
NaBr	...	2.2	...	...	...	...	2.3	...	...	...

72. Bliss Van Auken Co., Saginaw, Mich. Composite natural brine from 3 wells, 80° by salimeter. 1911. R. F. Gardner, analyst.

73. Edward Germain, Saginaw, Mich. Natural brine from well No. 1, 750 feet deep. 1910. R. F. Gardner, analyst.

74. Mershon, Eddy, Parker & Co., Saginaw, Mich. Composite natural brine from 2 wells. 1911. R. F. Gardner, analyst.

75. S. L. Eastman Flooring Co., Saginaw, Mich. Composite natural brine from 2 wells, 80° by salimeter. 1911. R. F. Gardner, analyst.

76. Saginaw Plate Glass Co., Saginaw, Mich. Composite brine from 10 wells. 1911. R. F. Gardner, analyst.

77. Dow Chemical Co., Midland, Mich. Composite brine from 10 wells. 1911. R. F. Gardner, analyst.

78. Dow Chemical Co., Mt. Pleasant, Mich. Composite brine from 5 wells. 1911. R. F. Gardner, analyst.

79. Saginaw Salt Co., St. Charles, Mich. Brine from one well. 1911. R. F. Gardner, analyst.

80. Saginaw Salt Co., St. Charles, Mich. Plant No. 2. Composite natural brine from 2 wells. 1911. R. F. Gardner, analyst.

81. Port Huron Salt Co., Port Huron, Mich. Natural brine from a shallow well at plant. 1911. R. F. Gardner, analyst.

TABLE II.—NATURAL BRINES FROM OHIO AND WEST VIRGINIA.

B. of S. No.	82.	83.	84.	85.	86.	87.	88.	89.	90.
Serial No.	105.	108.	113.	114.	119.	121.	123.	125.	128.
K	3.2	3.2	5.8	3.9	0.2	0.2	1.0	trace	trace
Na	68.0	62.7	48.0	43.4	24.6	37.1	124.8	4.4	37.8
Ca	29.0	30.8	45.6	48.6	2.6	3.8	1.0	1.2	2.6
Mg	6.4	6.4	9.8	11.2	5.8	1.0	1.6	0.2	1.0
Cl	170.2	164.8	187.0	188.4	57.2	66.0	183.0	65.8	65.6
SO_4	0.6	trace	none	0.2	trace	trace	1.0	trace	trace
Br	0.2	2.0	0.4	...	0.6	1.6	...	1.8	...
Conventional Combinations.									
KCl	6.1	6.1	11.1	7.4	0.4	0.4	2.0	trace	trace
NaCl	172.6	159.1	121.8	109.7	62.4	92.8	289.6	104.1	95.9
$CaCl_2$	70.3	85.2	126.1	134.2	7.2	10.5	2.8	3.2	7.2
$MgCl_2$	23.9	14.9	36.8	43.9	19.6	3.9	6.3	0.8	3.9
Na_2SO_4	....	....	....	....	....	....	11.8	....	....
$CaSO_4$	2.0	trace	none	0.3	trace	trace	trace	trace	trace
$MgBr_2$	0.5	4.6	0.8	..	1.4	....	....	....	....
NaBr	....	....	....	....	....	2.1	....	2.3	....

82. Colonial Salt Co., Akron, Ohio. Natural brine occurring in strata above rock salt horizon. 1911. R. F. Gardner, analyst.

83. Columbia Chemical Co., Barberton, Ohio. Natural brine occurring above artificial brine horizon. 1911. R. F. Gardner, analyst.

84. Diamond Alkali Co., Fairport Harbor, Ohio. Natural brine occurring in strata 300 feet above rock salt horizon. 1911. R. F. Gardner, analyst.

85. Diamond Alkali Co., Fairport Harbor, Ohio. Natural brine. 1911. A. R. Merz, analyst.

86. Dixie Salt Works, Mason, West Va. Composite natural brine from 4 wells. 1911. R. F. Gardner, analyst.

87. Pomeroy Salt Association, Pomeroy, Ohio. Composite natural brine from 2 wells. 1911. R. F. Gardner, analyst.

88. Pomeroy Salt Association, Pomeroy, Ohio. Natural brine from spring. 1911. R. F. Gardner, analyst

89. Hartford City Salt Co., Hartford, West Va. Composite natural brine from 5 wells. 1911. R. F. Gardner, analyst.

90. Liverpool Salt Co., Hartford City, West Va. Composite brine from 5 wells. 1911. R. F. Gardner, analyst.

TABLE III.—MISCELLANEOUS NATURAL BRINES.

B. of S. No.	91.	92.	93.	94.	95.	96.
Serial No.	13.	39.	46.	49.	55.	62.
K	0.1	0.2	0.4	0.2	0.2	0.1
Na	19.3	114.4	112.1	2.1	44.5	15.5
Ca	4.4	1.8	7.6	trace	8.2	1.2
Mg	1.4	1.0	1.2	slight trace	trace	1.8
Cl	39.5	179.4	185.8	3.4	83.2	28.2
SO_4	0.4	3.6	3.8	trace	trace	4.2
Br	0.7	trace	0.4	none	none	none
Conventional Combinations.						
KCl	0.2	0.4	0.8	0.4	0.4	0.2
NaCl	49.0	290.3	284.5	5.3	113.0	34.2
$CaCl_2$	11.6	0.8	16.6	trace	22.7	3.3
$MgCl_2$	3.1	3.8	3.1	slight trace	trace	7.1
Na_2SO_4	...	...	...	...	...	6.2
$CaSO_4$	0.6	5.1	5.4	trace	trace	trace
$MgSO_4$	....	....	....	....	....	....
$MgBr_2$	1.3	trace	0.8	none	none	none

91. J. J. Dickinson & Co., Malden, W. Va. Natural brine from one well, 1000 feet deep. 1910. R. F. Gardner, analyst.

92. Grand Saline Salt Co., Saline, Texas. Natural brine direct from well. 1910. R. F. Gardner, analyst.

93. W. H. Chaney, Salton, Okla. Brine from spring. 1910. R. F. Gardner, analyst.

94. N. V. V. Franchot (Olean, N. Y.), Indian Creek, McKean Co., Penn. Natural brine from one well, 1100 feet deep. 1910. R. F. Gardner, analyst.

95. Pine Oil Co., Sistersville, W. Va. Natural brine from one well, 1250 feet deep. 1910. R. F. Gardner, analyst.

96. New Domain Oil and Gas Co. (Lexington, Ky.), Griffin, Wayne Co., Ky. Natural brine from one well, 300 feet deep, above oil sand. 1910. R. F. Gardner, analyst.

TABLE IV.—BITTERNS FROM NATURAL BRINES OF MICHIGAN.

B. of S. No.	97.	98.	99.	100.	101.	102.	103.	104.	105.	106.
Serial No.	63.	65.	67.	69.	74.	75.	80.	81.	85.	89.
K	1.3	1.6	4.2	2.6	0.3	10.2	1.2	0.2	trace	trace
Na	66.1	83.3	78.2	76.1	1.0	42.1	52.5	0.1	60.9	119.9
Ca	40.6	32.4	36.4	32.8	18.9	192.6	50.2	18.4	0.6	1.8
Mg	11.5	9.6	11.0	9.6	4.6	35.2	11.6	3.4	0.4	trace
Cl	207.7	198.4	202.2	195.8	43.9	427.8	205.4	42.6	91.5	184.2
SO_4	0.4	trace	0.8	1.4	none	none	0.6	none	3.6	4.8
Br		4.4	3.3	2.2	1.1	trace	trace	none	4.3	trace
					Conventional Combinations.					
KCl	2.5	3.1	8.0	5.0	0.6	19.5	2.3	0.4	trace	trace
NaCl	167.5	211.6	198.4	193.0	2.5	106.9	133.3	0.3	147.2	298.6
$CaCl_2$	111.8	89.6	99.8	89.1	51.4	532.6	138.0	50.6	1.7	5.0
$MgCl_2$	45.1	15.3	19.3	26.3	12.5	18.4	45.5	13.3	1.6	trace
								$CaHCO_3$		
Na_2SO_4	....	....	....	....	....	....	....	0.4	5.3	7.1
$CaSO_4$	0.6	trace	1.1	2.0	none	none	0.9	none	trace	trace
					$CaCO_3$		F_2Cl_6			
$MgSO_4$	....	....	....	....	0.9	....	2.3	....	....	....
$MgBr_2$	....	10.1	9.5	5.1	2.5	trace	trace	none	....	trace
					H_2O			H_2O		
NaBr	....	....	....	....	29.6	....	....	35.0	5.5	....

97. Hine & Co., Bay City, Mich. Bittern from grainer, 5 days' evaporation. 1911. A. R. Merz, analyst.

98. Bliss, Van Auken Co., Saginaw, Mich. Bittern from grainer, 5 days' evaporation. 1911. R. F. Gardner, analyst.

99. Edward Germain, Saginaw, Mich. Bittern from grainer, 14 days' evaporation. 1911. R. F. Gardner, analyst.

100. Mershon, Eddy, Parker Co., Saginaw, Mich. Bittern from grainer, 4 days' evaporation. 1911. R. F. Gardner, analyst.

101. Saginaw Chemical Works (Saginaw Plate Glass Co.), Saginaw, Mich. Solid calcium chloride; results in per cent. Contains also trace of barium and strontium. 1911. R. F. Gardner, analyst.

102. Saginaw Chemical Works (Saginaw Plate Glass Co.), Saginaw, Mich. Bittern, which had been evaporated to 8.5 per cent. of the volume of the original brine, before the final evaporation for the preparation of calcium chloride. Sample was taken while hot. On cooling, a crystalline solid separated which contained 1.1 per cent. potassium, or 2.3 per cent. potassium chloride. 1911. R. F. Gardner, analyst.

103. Dow Chemical Co., Mt. Pleasant, Mich. Bittern after removal of bromine. Contaminated with iron compounds. 1911. R. F. Gardner, analyst.

104. Van Schaack Calcium Works, Mt. Pleasant, Mich. Solid calcium chloride; results in per cent. 1911. R. F. Gardner, analyst.

105. Saginaw Salt Co., St. Charles, Mich. Bittern, 4 days' evaporation. 1911. R. F. Gardner, analyst.

106. Port Huron Salt Co., Port Huron, Mich. Bittern from grainer. 2 weeks' evaporation. 1911. R. F. Gardner, analyst.

TABLE V.—BITTERNS FROM NATURAL BRINES OF OHIO AND WEST VIRGINIA.

B. of S. No.	107.	108.	109	110.	111.	112.	113.
Serial No.	122.	131.	51.	120.	127.	129.	130.
K	3.2	0.7	0.4	2.7	trace	2.9	0.8
Na	2.6	0.6	97.3	....	3.7	....	2.4
Ca	145.2	19.5	16.2	135.8	18.5	143.4	19.6
Mg	42.4	4.9	4.8	48.4	5.3	43.4	5.1
Cl	348.8	50.4	191.2	355.2	53.9	346.4	53.9
SO_4	5.2	none	1.8	4.8	none	3.8	none
		H_2O					
Br	11.6	23.9	none	11.0	trace	12.2	none
			Conventional Combinations.				
KCl	6.6	1.4	0.8	5.4	trace	5.8	1.5
NaCl	6.7	1.6	246.9	8.4	9.4	0.7	6.1
$CaCl_2$	337.9	53.9	42.6	362.5	51.2	379.0	54.2
$MgCl_2$	158.6	19.2	188.8	179.2	20.8	162.5	20.0
					H_2O		H_2O
Na_2SO_4	....	....	....	....	18.6	....	18.2
$CaSO_4$	7.3	none	2.6	6.8	none	5.3	none
$MgBr_2$	13.3	H_2O	none	12.6	....	14.1	none
		32.9					
NaBr	....	....	....	....	trace	....	....

107. Pomeroy Salt Association, Pomeroy, Ohio. Bittern before going to bromine salts. 1911. A. R. Merz and R. F. Gardner, analysts.

108. Eureka Calcium Works, Pomeroy, Ohio. Calcium chloride; results in per cent. 1911. R. F. Gardner, analyst.

109. Hartford City Salt Co., Hartford, W. Va. Bittern. 1910. R. F. Gardner, analyst.

110. Dixie Salt Works, Mason, W. Va. Bittern before going to bromine stills. 1911. A. R. Merz and R. F. Gardner, analysts.

111. Hartford City Salt Co., Hartford, W. Va. Solid calcium chloride; results in per cent. 1911. R. F. Gardner, analyst.

112. Liverpool Salt & Coal Co., Hartford, W. Va. Bittern before going to bromine stills. 1911. A. R. Merz and R. F. Gardner analysts.

113. Liverpool Salt & Coal Co., Hartford, W. Va. Solid calcium chloride; results in per cent. 1911. R. F. Gardner, analyst.

A large number of natural brines of Ohio have been analyzed by Wormley;[1] these analyses are of especial interest in that, unlike most analyses of American salines recorded in the literature, they have included the determination of potassium salts.

[1] Geol. Survey Ohio, II., 601–2 (1874).

DISCUSSION OF RESULTS.

A comparison of the natural brines with the artificial shows that the former are purer solutions of sodium chloride than the latter. This is to be expected from *a priori* consideration. The natural brines in their migration through porous strata would

tend to become contaminated with any soluble materials encountered.

The most striking difference between the two lies in their respective calcium content. Natural brines are comparatively rich in calcium (and magnesium), while the calcium content of the artificial brines represents but little more than the solubility of calcium sulphate in that solution.

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THE DETERMINATION OF ZINC BY ELECTROANALYSIS.[1]

By ELLWOOD B. SPEAR AND SAMUEL S. STRAHAN.

The electrolytic determination of zinc has been attended by unsatisfactory results because many of the vital conditions were not known and many of the causes of deleterious effects not clearly understood. Two years ago an article was published[2] by one of us on the causes of the high results so frequently obtained, and in another article[3] the statement was made that our experiences with the potassium and sodium hydroxide methods were unsatisfactory. Some time later Kemmerer[4] published very fair results, having used a rapid method with KOH. This method is, with the slight modifications we have introduced, one of the very best for the determination of zinc.

Our modifications consist in: *First*, cooling the solution a few minutes before the end of the experiment. *Second*, reducing the amount of the KOH employed. The reasons for these changes are discussed below. We have also carefully investigated the various causes of error in the employment of this method. These causes will be considered later. The procedure itself is as follows:

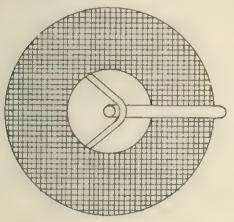

FIG. 1.

FIG. 2.

The zinc to be determined, preferably about 0.4 gram, must be in the form of sulfate. Nitrates and ammonium salts must be absent. Very little free sulphuric acid should be present, because potassium sulphate, which is formed when the acid is neutralized with the hydroxide, is not very soluble in strongly alkaline solution: 10 to 25 grams KOH are dissolved in water and the total volume of the electrolyte made up to 125 cc. The solution is brought almost to the boiling point and electrolyzed with a normal current density of 3 amperes. A rotating platinum anode and stationary nickel gauze cathode may be used, but we strongly recommend a rotating nickel gauze cathode (see Fig. 1) and a stationary platinum plate or spiral anode. The cathode must be kept completely buried in the solution. The anode should be placed above and never at the side of the cathode. The time required for complete precipitation varies, of course, with the size of the cathode. With a cathode area of 100 sq. cm. the time necessary was 45 minutes, using 25 grams KOH, and 30 minutes using only 12 grams.

Seven to eight minutes before the end of the experiment, the anode and the inside of the beaker should be washed down with a small amount of water from a wash bottle in order to obtain any zinc that may have crept up owing to frothing or stirring. This is a precaution that should always be taken in electroanalysis.

Five to six minutes before removing the electrodes the solution should be cooled, with ice if necessary, to below 25° C. The solution should be lowered from the electrodes without interrupting the current. The cathode should be quickly but thoroughly washed first with *water*, then with *alcohol*, and finally with *ether that has been very recently dried over sodium and freshly distilled*. The ether should be immediately dried off the cathode by gentle heating and the electrode weighed after standing for one-half hour in a desiccator.

TABLE I.

No.	Grams of zinc. Taken.	Found.
1	0.3946	0.3943
2	0.3946	0.3948
3	0.3946	0.3949
4	0.3946	0.3947
5	0.3946	0.3949
6	0.3946	0.3955
7	0.3946	0.3945
8	0.3946	0.3942

TABLE II.

No.	Grams of zinc. Taken.	Found.
1	0.3946	0.3946
2	0.3946	0.3948
3	0.3946	0.3952
4	0.3946	0.3952
5	0.3946	0.3950
6	0.3946	0.3943
7	0.3946	0.3947
8	0.3946	0.3951

The method is capable of giving very good results, but this is due to a compensation of errors. When the deposit is washed with water some zinc is always lost in the wash water, while some zinc hydroxide is formed at the same time on the electrode. These two amounts are small and very closely counterbalance each other. In Tables I and II we give 16 consecutive results, using 25 and 12 grams KOH, respectively. The results were not all obtained on the same day nor by the same experimenter.

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

[2] *J. Am. Chem. Soc.*, **32**, 533.

[3] *Ibid.*, **32**, 532.

[4] THIS JOURNAL, **2**, 375.

PREPARATION OF THE SOLUTIONS FOR THE INVESTIGATION.

Zinc Sulphate.—About 4 grams C. P. zinc, the purity of which had been verified by a careful analysis, were dissolved in nitric acid, slightly more than the requisite amount of concentrated sulphuric acid was added and the whole evaporated to dryness over a water bath. The resulting zinc sulphate was dissolved in water and the solution made up to 250 cc. in a carefully calibrated flask.

Potassium Hydroxide.—Two hundred and fifty grams KOH of good quality were dissolved in water and the solution made up to one liter.

Solution for Analysis.—Twenty-five cc. of the zinc sulphate solution from a carefully calibrated pipette were added to 100 cc. of the prepared KOH in a deep 250 cc. beaker. For the analyses using a lesser amount of KOH, 50 cc. of the solution and 50 cc. water were taken. The solution was brought almost to the boiling point and at once electrolyzed. Zinc deposits from hot KOH have a much more metallic appearance than those from a cold solution and in the latter case the results are always too high. The solution must not contain nitrates, else all the zinc cannot be thrown down. One gram of potassium nitrate will almost completely prevent the deposition of the zinc. We have not yet investigated the cause for this.

THE ELECTRODES AND THEIR MANIPULATION.

Cathode.—Many copper, platinum and nickel cathodes of various shapes were tried and the most satisfactory was found to be one of our own design, as shown in Fig. 1. It is made of nickel gauze, 30 mesh to the inch, with a stout wire standard of the same material. The gauze should not continue to the center to meet the stem because the rotating motion given to the solution sometimes causes the center to become exposed to the air and some of the freshly deposited zinc is oxidized to zinc hydroxide. If zinc is deposited electrolytically and any portion of the deposit exposed to the air a white ring of zinc hydroxide can be seen on the upper edges. Our investigation showed that the deposits always weighs 2–4 mg. too much, provided that the cathode protruded above the solution. This fact doubtless explains some of the high results obtained by many experimenters.

The upper edge of the cathode should be turned in toward the center, dome-shaped, for, as the anode is placed above the cathode for reasons given below, most of the deposition will take place on the extreme upper edge, become bad and fall off if the cathode is shaped as shown in Fig. 2. The cathode was rotated at the rate of 400 revolutions per minute. A rotating cathode is preferable to a rotating anode, because in the former case a much better stirring effect on the immediate surface of the cathode is obtained. Copper cathodes are not suitable because they oxidize somewhat in hot solution and thus introduce an error. Platinum cathodes do not give as good zinc deposits as nickel, possibly because of the difference in polarization effects on these two metals.

Anode.—As already indicated, the anode may be a platinum plate or spiral. The object in placing the anode above the cathode is to prevent the oxidation of the deposit by the gases liberated by the current. It was found by experiment that the rate of deposition was very much slower, and that it was almost impossible to get all the zinc out if the anode were placed by the side of and close to the cathode. This is an excellent confirmation of the theory pointed out by one of us in an article elsewhere on oxidation processes at the cathode.[1]

The solution should be cooled for the last 5–6 minutes, with ice if necessary, in order that the temperature of the liquid may not be above 25° C., when the cathode is removed. At the moment of lowering the solution, the cathode is covered with a layer of KOH, which rapidly attacks the deposit if the temperature is above 25° C. Some of the zinc would be dissolved and potassium zincate be formed. When the cathode is washed, most of this comes off and zinc is thus lost in the wash water. Even when the temperature is low some zinc is found in the washings, but the amount is fortunately small. On the other hand, the solution must not be cooled too long before the end, otherwise the character of the deposit is affected.

The cathode must be washed thoroughly by rotating it in water to get rid of the KOH. The water should be cold and the work should be done with despatch or an appreciable amount of zinc hydroxide will be formed, thus invalidating the determination. The deposit should next be dipped into alcohol and finally thoroughly wet with ether that has been dried over sodium. Washing with alcohol and ether alone will not remove all the KOH, and the results will be high if water is not used. The deposit should be immediately dried over a heated surface or free flame. The ether must not be allowed to evaporate off in the air nor in a desiccator, else the metal, cooled below the temperature of the surroundings, will be covered with a film of moisture that will attack the deposit, form zinc hydroxide, and therefore increase the weight. This was shown experimentally by treating the previously dried and weighed deposits with ether, allowing them to stand in a desiccator until dry, and reweighing. Each treatment caused an increase of from 2 to 6 tenths of a milligram. It is unwise to heat the deposit much above the temperature of the surroundings. If the ether is not recently dried and distilled it contains water and oxides that attack the freshly deposited zinc.

It is obvious that the naked cathode should be treated in precisely the same manner before the electrolysis in which the deposit is to be made as when the precipitation is completed.

The endeavor was made to prevent the loss of zinc in the wash water *first*, by siphoning off the KOH solution and gradually replacing it with water; and *second*, by making the wash water a conductor with a few drops of KOH and allowing the current to pass

[1] "The Coprecipitation of Copper and Carbon by Electrolysis; Oxidation at the Cathode." Original Communications Eighth International Congress of Applied Chemistry, Vol. 21, p. 93.

through while the cathode was being washed. The first method proved a failure because zinc is continuously redissolved, even during the passage of the current. A portion of this zinc was unavoidably siphoned off and lost. Employing the second method, we succeeded in getting all the zinc on the electrode, but the results were invariably from 2–4 mg. too high. This increase in weight was doubtless due to the presence of zinc hydroxide formed by the action of water on the deposit.

Our investigations embraced a large number of experiments and 180 quantitative determinations.

SUMMARY.

In this article we have introduced certain modifications of the potassium hydroxide method and shown that it is reliable for the electrolytic determination of zinc.

We have shown that this method entails a compensation of errors.

A new cathode has been devised and recommended for use in electroanalysis.

The following sources of errors have been investigated and pointed out:

1. The loss of zinc in the wash water, counterbalanced by the formation o zinc hydroxide on the cathode.
2. The effect of air on an exposed cathode.
3. The oxidation of the deposit by anode gases.
4. The effect of temperature at the beginning and end of the electrolysis.
5. The effect of ether containing water and oxides on the deposit.
6. The high results obtained by letting the ether evaporate off the cathode in a desiccator.
7. The presence of nitrates.

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THE KAMBARA EARTH. A DECOLORIZING MATERIAL FOR MINERAL OILS, ETC.

By K. KOBAYASHI.

Received Sept. 18, 1912.

The production of Kambara earth in Japan has greatly increased in the last three years. The chief source of the material is in the province of Echigo, though deposits of the earth belonging to this class have also been found in other provinces. Now the Kambara earth is largely used as the decolorizing material for mineral oils, especially for neutral oil and lubricating oil. There are massive deposits of very pure Kambara earth near Uchikura River, three miles southeast of the city of Shibata, Kambara, Echigo. I have found two other deposits of the earth, one in the province of Fukushima, and the other in the province of Ishikawa. I have investigated this earth since 1892, and found that it belongs to the class of Fuller's earth in England and Florida earth in the United States of America.

The Kambara earth in these deposits is simply dug out, dried in iron pans, ground with iron stamps, and used after levigation treatment. This Kambara earth occurs usually in massive state, with white or yellowish color, sometimes bluish or sometimes greenish.

PHYSICAL AND CHEMICAL PROPERTIES OF THE KAMBARA EARTH.

(1) *Outward Appearance.*—The Kambara earth resembles hard wax, in the outward appearances, is soapy to the touch and is strongly detergent, absorbing grease and oil. It is easily dissociated by and miscible with water. A fine powder of the earth has no soapy feeling as the powder of steatite or soapstone has. The paste of the earth made with water shows no adhesiveness between particles. The decolorizing action of the earth may be promoted by heating it to 100°–150° C. But if the earth is heated to red heat, it loses its combined water and at the same time its suitability as a decolorizing agent is destroyed.

(2) *Degree of Fineness of the Earth.*—The Kambara earth consists of very fine particles of the earth and has no crystalline particles of quartz in it. The classification by sifting shows clearly this fact.

	Under 0.1 mm.	0.1–0.25 mm.	0.25–0.5 mm.	Above 0.5 mm.
Kambara earth (Echigo)	29.3	69.2	1.5	0
Kambara earth (Fukushima)	25.0	73.5	1.5	0
Kambara earth (Ishikawa)	24.2	73.5	2.3	0
Kaolin (Owari)	14.5	36.4	23.6	25.5
Kaolin (Owari)	7.1	21.2	35.5	26.2
Steatite (Harima)	0.5	38.8	38.5	22.2

From these results it will be understood that there is a great difference in fineness between Kambara earth and other kaolins. Its suitability as a decolorizing agent, as a matter of fact, depends upon the degree of fineness.

(3) *The Chemical Composition of the Earth.*—The following analysis shows the composition of the earth:

	Kambara earth.			Clay.		
Percentages.	Echigo	Fukushima.	Ishikawa.	Kaolin.	Kaolin.	Steatite.
SiO_2	60.71	63.17	58.11	68.60	47.20	71.94
Al_2O_3	13.18	13.23	20.86	21.23	34.61	21.41
Fe_2O_3	3.68	2.20	1.04	1.00	1.05	0.45
CaO	0.62	1.44	0.56	0.10	0.21	0.31
MgO	0.38	1.09	1.20	0.42	0.26	0.23
$Na_2O + K_2O$	1.54	0.42	0.50	0.52	0.58	0.75
Loss on ignition	20.04	17.95	18.58	7.93	16.17	5.01
Loss on heating to 110° C.	14.72	11.41	10.37	...	...	...

From the above analytical point of view, we cannot distinguish the Kambara earth from kaolin or steatite, but we can do it by the determination of the hydrates of silica in it. According to Mr. D. T. Day, the analytical results on Fuller's earth and Florida earth are as follows:

	Fuller's earth. Yellowish.	Fuller's earth. Bluish.	Florida earth.	Dakota earth.
SiO_2	59.37	52.81	56.73	58.72
Al_2O_3	11.82	16.92	27.78	16.90
Fe_2O_3	6.27	3.78	3.21	4.00
CaO	6.17	7.40	0.81	4.06
MgO	2.09	2.27	0.64	2.56
$Na_2O + K_2O$	0.99	0.79	....	2.11
Loss on ignition	13.19	14.29	19.52	8.10

He defines Fuller's earth in the following words: "Fuller's earth seems to be a high percentage of silica, occasionally as much as from 65 per cent. to 70 per

cent., and water, in the sun-dried material, from 15 per cent. to 25 per cent., of which only about one-half is expelled at 100° C."

(4) *Hydrates of Silica in the Earth.*—It seems to be the case that the Kambara earth is essentially composed of hydrates of silica accompanied by aluminum silicate. Weigh out exactly 1 gram of the earth into a platinum basin and add 50 cc. of caustic soda solution (sp. gr. 1.115) and boil it for five hours. In this treatment one portion of the earth will be dissolved in the alkali solution. Filter the solution, wash thoroughly with hot water, add the washings to the main portion of the liquid and determine the silica in this filtrate by the usually known analytical method. This determination will show the percentage of silica which existed in the earth in a form of certain hydrates of silica. My analytical results were as follows:

	SiO_2 as hydrates of silica. Per cent.
Kambara earth (Echigo)	29.35
" (Fukushima)	24.54
" (Ishikawa)	18.03
Fuller's earth	24.72
Kaolin	6.62
Steatite	2.93

Kaolin and steatite do not contain so much hydrates of silica as the Kambara earth. I have determined the amount of water in the Kambara earth dried at different temperatures, namely, loss of weight under 100° C. = 12.43 per cent.; 100° C. to 200° C. = 2.44 per cent.; 200° C. to 250° C. = 2.66 per cent.; red heat = 6.69 per cent.

The suitability of this earth as a decolorizing agent for oils mainly depends upon the higher percentage of the hydrates of silica, probably having the formula of $3SiO_2.2H_2O$.

(5) *The Kambara Earth is Weakly Acidic.*—The samples employed for the following tests were finely powdered, dried in a steam bath, and sifted to the same grade of fineness.

Experiment A.—The Kambara earth was placed upon a piece of blue litmus paper and moistened with water; the color changed to red at the spot of contact.

Experiment B.—Ten cc. of a solution of methyl orange were placed in a test tube and 1 gram of the sample added and shaken violently. The color of the samples was observed after standing for one hour.

	Color of solution.	Color of earth.
Kambara earth (Echigo)	Decolorized	Pink
" (Fukushima)	"	"
" (Ishikawa)	"	"
Fuller's earth	"	"
Kaolin (No. 1)	Not decolorized	Original color
Steatite	"	"
Kaolin (No. 2)	"	"
Kambara earth heated to 100° C.	Decolorized	Pink
Kambara earth heated to 200° C.	"	"
Kambara earth heated to red heat	Not decolorized	Original color

In the case of litmus solution, the Kambara earth decolorized the solution and the earth itself became a wine-red color.

From the above results we know that there is a great difference between the Kambara earth and ordinary kaolin and steatite, with respect to their action on indicators.

Experiment C.—Ten grams of the Kambara earth were weighed out into a flask and about 100 cc. of distilled water added. It was boiled for 10 hours connected to a reflux condenser. The liquid was allowed to stand for 10 minutes after digestion and filtered. The filtrate had then no more action upon the above indicators. This filtrate contained a small quantity of sodium chloride.

(6) *The Kambara Earth Acts on an Alcoholic Solution of Guaiacum Resin.*—About 2 grams of guaiacum resin were taken in a glass-stoppered bottle and 300 cc. of absolute alcohol added. This was kept in a cool, dark place after stirring violently. By filtering the same, a pale brown tincture was obtained: 25 cc. of this tincture were placed in a small Erlenmeyer flask and 3 grams of each sample added.

	Color of solution.	Color of earth.
Kambara earth (Echigo)	Decolorized	Green color
" (Fukushima)	"	Pale green
" (Ishikawa)	"	"
Fuller's earth	"	"
Kaolin (No. 1)	Not decolorized	Original color
" (No. 2)	"	"
Steatite	"	"

From these results it seems to be the case that the action of the Kambara earth is not only of a physical but also of a chemical nature.

(7) *The Kambara Earth Acts on a Solution of Aniline Sulphate.*—The Kambara earth decolorizes a 1 per cent. solution of aniline sulphate and earth itself becomes a dark green color. Kaolin and steatite are not thus affected.

(8) *The Kambara Earth Decolorizes a Solution of Basic Dyestuffs.*—

Experiment A.—On Rhodamine solution. The color of the Rhodamine solution which is reddish brown with a greenish fluorescence is changed to pink by an acid. If the Kambara earth was added into the solution, the earth absorbed the color and the earth became pinkish in color.

Experiment B.—On Magenta powder. If about equal parts of a finely powdered magenta and Kambara earth were placed in an agate mortar and mixed well, the color of the mixture changed gradually. If we used kaolin instead of the Kambara earth there was no such change of color.

Experiment C.—On Malachite green solution. The Kambara earth absorbed, the color of the solution became dark green.

Experiment D.—On Benzoazoline. A Benzoazoline solution, which is bluish purple in color, is changed to red by the addition of a drop of alkali solution. The Kambara earth absorbed, this color became a violet color.

Besides the above mentioned dyestuffs, I also tested Benzo-brown BX, Delta purplin, Benzo black and Congo red.

In all those cases the Kambara earth absorbed the color of the solution of the dyestuff and it reacted chemically as a weak acid, while clays that do not belong to the Kambara earth type did not react toward those dyestuffs.

(9) *Action of Native Hydrates of Silica and Precipitated Hydrates of Silica on Litmus.*

Experiment A.—If hydrochloric acid is added drop by drop to a solution of sodium silicate with constant stirring it will, as is well known, give the gelatinous precipitate of orthosilicic acid (H_4SiO_4). This colorless gelatinous substance does not affect the color of litmus and possesses no resemblance in common with Kambara earth provided it is dried for one hour.

Experiment B.—If carbon dioxide gas is passed into the solution of water glass, a white precipitate of hydrate of silica will be produced. This precipitate, after drying, also does not affect the color of litmus.

Experiment C.—If one part of powdered glass, two parts of cryolite and four parts of concentrated H_2SO_4 are placed in a flask and heated gently, hydrofluosilicic acid gas will be produced. When this gas is passed into distilled water in a flask, white featherlike hydrate of silica will be obtained. I have examined this and also the action of fine powders of quartz, flint, rock crystal, chalcedony, opal and hyalite on the solution of indicators, etc. But all such substances do not decolorize the solution of indicators and have no resemblance to the Kambara earth.

(10) *On the Crude Oils and Distillates.*—The Kambara earth has a great decolorizing action on crude oil and its distillates. The earth absorbs the unsaturated hydrocarbons. I have determined the iodine absorption value of distillates of kerosene by Hübl's method.

		Before treatment.	After treatment.
"Chester" brand	(0.805).....	26.05	18.59
Japanese kerosene	(0.821).....	2.37	1.60
Japanese kerosene	(0.815).....	1.51	1.15

To cite a concrete example, the Higashiyama crude oil is of a very dark brown color and has a somewhat offensive smell. Its specific gravity is 0.8971 at 15.5° C. The Nishiyama crude oil is green in color, with a specific gravity of 0.8953 at 15.5° C. If we treat the former crude oil with the earth, then the color of it is changed to as dark green as the Nishiyama crude oil.

The properties of the Kitano crude oil differ widely from the above two petroleums. The oil is of lampblack brown color and its specific gravity is 0.871 at 15.5° C. The following results by filtration with the Kambara earth were obtained: 15 per cent., sp. gr. 0.850; next 10 per cent., sp. gr. 0.855; next 12.5 per cent., sp. gr. 0.860; next 17.5 per cent., sp. gr. 0.870. The first two filtrates were of amber color and the last two pale brown.

CONCLUSION.

Messrs. Engler and Albrecht investigated Florida earth and Fuller's earth and ascribed their action to their physical properties.[1] Messrs. D. T. Day and Richardson have also the same opinion. But I have found that Kambara earth acts as a weak acid. I think that the action of the earths depends upon both their physical and their chemical action. The tests to be made for the Kambara earths, in the order of their importance, are: Acidity, fineness, determination of hydrates of silica, determination of loss by weight on ignition, action upon guaiac resin solution, and also practical decolorizing action on standard oils.

I am at present investigating the action of the Kambara earth on the products from the dry distillation of wood and have found that not only some impurities in methyl alcohol and ketone can be removed by means of the Kambara earth, but that the earth is also applicable for separation of tar from pyroligneous acid. No doubt, the Kambara earth is in the same class with Fuller's earth, but the Kambara earth is the more efficient decolorizing agent. The Kambara earth is the most important substance for purification of mineral, animal and vegetable oils, and can also be used for the purification of some alcohols and ketones. I think it will be very convenient to give the name "acid earth" to all such earths and thus distinguish them from the ordinary kaolin and clay.

TOKYO, JAPAN.

[1] *Z. angew. Chem.*, **36**, 889 (1901).

INVESTIGATION OF THE METHODS FOR THE DETERMINATIONS OF TOTAL FATTY ACIDS IN COTTON-SEED FOOTS.[1]

By FRANK N. SMALLEY.

Recent coöperative work conducted by the Society of Cotton Products Analysts on the relative solvent power of gasoline of different boiling points when used in the determination of total fatty acids of cotton-seed foots by the Official Method of the Interstate Crushers Association, show such non-agreeing results, that the author believed that an investigation of the Official method to determine the reason for the wide discrepancies between the different chemists, and a study of the proposed substitute methods for the same, would be of value.

It might be well to state that the coöperative work brought forth the fact that all gasoline whose boiling points did not exceed 75° C. showed no differences in their solvent power. And as the greatest differences between any one chemist's reported values using the three grades of gasoline (boiling under 50°, from 50° to 65°, from 65° to 75°) was fifty-six hundredths of one per cent., while the greatest difference between the different chemists using the same grade of gasoline was 5.34 per cent., the author believed that the differences were due to the different chemists using different modifications of the official method.

The following is the Official Interstate Method: Weigh out eight to ten grams of the well-mixed sample into a small extraction flask. Saponify with an alcoholic solution of sodium hydroxide over a steam bath and heat with occasional stirring until all the alcohol is driven off. Wash out the soap with about 400 cc. of hot water into a beaker and digest on a water bath until complete solution of the soap is effected. Acidify with dilute sulphuric acid and continue heating on the water bath until the layer of fatty acids has melted clear. Cool and filter off the liquid from the cake of fatty acids, washing with cold water until no traces of sulphuric acid are left. Allow the fatty acids to

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

dry, most conveniently over night. Transfer the fatty acids to a folded filter paper and place in a Soxhlet extraction apparatus and dissolve the fatty acids adhering to the beaker with warm petrolic ether boiling below 50 degrees centigrade and extract with petrolic ether boiling below 50 degrees centigrade for three hours. Evaporate off the ether and heat to constant weight. Calculate percentage on original weight.

When this method was followed as closely as possible the author obtained values of 95.70 and 95.63, average 95.66 per cent. In this method the cake of crude fat was dissolved by extraction, care being taken to transfer from the beaker as much as possible of the same to the filter paper.

(1) A modification of the method of extracting was carried out as follows: The bulk of the crude fat was retained in the beaker and successively treated with 25 cc. portions of warm gasoline, each portion being filtered through the original filter paper, into the extraction flask, until the beaker was thoroughly cleaned; the filter paper now extracted in a Soxhlet apparatus, as before, gave the values of 95.33 and 95.38, average 95.36 per cent.

(2) A third method of extracting was carried out as follows: The whole of the crude fat, filter paper included, was treated with 100 cc. of gasoline in the original beaker and complete solution obtained by a few minutes' boiling over an electric hot plate. This was then filtered through a fresh filter paper into the extraction flask and the residue treated in the same manner with a fresh portion of gasoline and finally transferred to the filter paper which was extracted as before. This method gave results of 94.55 and 94.63, average 94.59 per cent.

In the first two extraction methods it was noticed that in the extracted solutions before evaporation there was a flocculent precipitate while the solution from the last method was perfectly clear, showing that a saturated solution of the crude fat in gasoline dissolves resins and coloring matter which are precipitated out on dilution of the same. While the differences between these three methods is only one and seven-hundredths per cent. the author believes that this is the particular point in the method which has caused the wide differences in the results of the previously mentioned coöperative work.

The following is one of the methods which has been proposed as a substitute: Weigh out accurately into a tared beaker of 300 cc. capacity four to five grams of the thoroughly mixed sample and treat as follows: 10 to 12 cc. of 40° B. caustic soda and 15 to 20 cc. of 95 per cent. alcohol are added and the whole mass thoroughly stirred. The beaker is then placed on a sand bath, the temperature of which is so regulated that the evaporation is not too rapid or violent and the mass stirred repeatedly. When the mass is nearly dry the sides of the beaker are washed down with a few cc. of alcohol and the evaporation continued until the alcohol is expelled and the soap nearly dry. The beaker and contents are then removed from the sand bath and allowed to cool. The soap is then thoroughly dissolved in about 200 cc. of boiling water and decomposed by adding dilute sulphuric acid in considerable excess. The beaker and contents are again heated on the sand bath until the fatty acids become clear. While still hot the contents of the beaker are filtered through a filter, previously wet with hot water, care being taken to hold back the larger part of the fatty acids until the water has filtered through. The fatty acids are then transferred to the filter, the beaker and fatty acids thoroughly washed with boiling water. The filter is allowed to drain for fifteen minutes and is then transferred to the original beaker in which the saponification was made and the whole set in a steam oven for 15 or 20 minutes to expel moisture. When thoroughly dry, which is shown by the saturation of the filter paper by the fatty acids, the fatty acids are dissolved in gasoline (distilling under 50° C.) and filtered through a clean, dry filter (but using the same funnel used in the previous filtration of the fatty acids from the acid solution) into a 6 oz. flask, care being taken to wash beaker and funnel free from fatty acids. At least 100 to 125 cc. of gasoline should be used in dissolving the fatty acids and washing the beaker and funnel. The solution of fatty acids in gasoline is then placed on a steam bath (with air jet) until the gasoline is completely expelled after which the flask and fatty acids are dried in an oven at 105° C. for 15 minutes. The flask is then removed from the oven and allowed to cool (the fatty acids crystallizing), after which the whole is weighed. From these weights the percentage of fatty acids is calculated. Two tests on each sample are run and the duplicate results should check within 0.25 per cent. or less. The essential difference is the manner of separating fatty acids from the solution from which they are precipitated. It has been the author's experience that it is almost impossible to sufficiently wash the fat free from mineral acid without a small portion of the same passing through the filter paper. Oftentimes even an apparently clear filtrate when allowed to stand on the steam bath for some time will show small globules of fat. This, as well as the fact that drying in the oven with the mineral acid not thoroughly removed causes error, condemns the method in the opinion of the author.

A separatory funnel method was also tried in which the saponification, solution, and throwing out of the fatty acids was conducted just as in the official method. The solution was then placed in a separatory funnel and the extraction of the crude fat made by repeated treatments of gasoline, the various gasoline portions collected, filtered through dry paper, and the fat thoroughly removed from the same, and the gasoline evaporated and residual fat weighed. This method gave results as follows: 93.28; 92.10; 92.50; 92.98; 92.50 and 93.48. As these values show such differences among themselves, the highest showing much lower than our other method, the author considers method (1) which requires extreme care and considerable skill to manipulate, so that checking results may be obtained. With the best of care losses

occur, and furthermore the actual manipulating time is considerably increased. On these grounds the author considers that the method need not be considered as a substitute for the official method.

A number of other modifications of the official method consist of methods of saponification and of solution.

Therefore, the author concludes that the *most accurate method* is that of the *Official Interstate Method with the following modification:* For the solution of the crude fat, transfer the fatty acids on the filter paper back to the original beaker and dissolve by the addition of 100 cc. of gasoline with a few minutes' boiling on the electric hot plate. This is then filtered through dry paper and the residue treated with successive smaller portions of gasoline until the fat is thoroughly dissolved. In case only two such extractions are given, it is recommended that the filter paper with the residue be given an extraction in a Soxhlet apparatus.

SAVANNAH, GEORGIA.

THE DETERMINATION OF CHROMIUM AND VANADIUM IN STEEL.

By D. J. DEMOREST.

Received Sept. 17, 1912.

The writer recently described a method for the determination of vanadium in iron and steel,[1] in which the vanadium alone is determined. Since chromium is present in many vanadium steels it is desirable to determine chromium along with the vanadium, and the present paper describes a modification of the above mentioned method so as to easily determine the chromium and vanadium in the same sample. Nothing new is presented except that the details of the known method for chromium are worked out so that the author's method for vanadium can be combined with it.

The process is as follows: Two grams of the sample are dissolved in a 400 cc. flask by a mixture of 12 cc. strong sulphuric acid and 50 cc. of water. The flask is heated until solution is complete, when it is set off the hot plate and 25 cc. of nitric acid (sp. gr. 1.42) is very cautiously added. The iron is immediately oxidized to the ferric state with the evolution of much nitrous fumes. The solution is heated to boiling until the brown fumes are all driven off, then the flask is set off the hot plate and sodium bismuthate added until everything in solution is oxidized and the manganese appears as permanganic acid, which does not disappear on shaking. Now the solution is diluted to 200 cc., a little more sodium bismuthate added, and the solution boiled for 20 minutes to decompose the permanganic acid to manganese dioxide. It is then cooled by adding 50 cc. of water and filtered through asbestos. Then the volume is made up to 300 cc. and the solution cooled to tap water temperature, when it is ready for the chromium titration after the addition of 5 cc. of syrupy phosphoric acid to decolorize the iron.

To titrate, run in $N/100$ ferrous sulphate solution until all chromium and vanadium are reduced. This can be told by testing a drop on a white plate with a drop of ferricyanide. If a blue color is obtained, enough ferrous sulphate has been added. Then $N/100$ permanganate is added until a pink color appears, which persists on shaking, and a few cc. more are added and the solution is stirred for a minute. Then $N/100$ ferrous sulphate is added until the pink just disappears. The total ferrous sulphate minus the permanganate $\times$ 0.0001733 equals the chromium present.

Now to the solution enough ferrous sulphate to reduce the vanadium and a considerable excess is added, the solution mixed and about one gram of sized manganese dioxide is dropped in. The solution is shaken until a test with ferricyanide on a white plate shows that all ferrous iron has been oxidized. Then it is filtered through asbestos (using suction) and is ready for titration: $N/100$ permanganate is added until a persistent pink color is obtained, then several cc. more are added and the solution is shaken for a minute. Now $N/100$ ferrous sulfate is added until the pink just disappears. The permanganate used minus the ferrous sulphate used $\times$ 0.00051 equals the vanadium present.

Notes on the Process.—The bismuthate oxidizes the chromium, vanadium and manganese to chromic acid, vanadic acid and permanganic acid. Boiling destroys the permanganic acid and manganese dioxide precipitates and is filtered off. When ferrous sulphate is added, chromic and vanadic acids are reduced to trivalent chromium and quadrivalent vanadium; then when permanganate is added vanadium only is oxidized back and the ferrous sulphate minus the permanganate measures the chromium.

Vanadium is again reduced by ferrous sulphate (not measured), the excess of ferrous sulphate oxidized by manganese dioxide, leaving the vanadium ready to be titrated.

The manganese dioxide must not be too fine. It should settle perfectly clear in a beaker of water in 15 seconds. It must be natural or crystalline.

The following are some results obtained by the above method:

Percentages vanadium.		Percentages chromium.	
Present.	Found.	Present.	Found.
0.145	0.143	0.078	0.086
0.145	0.145	0.155	0.160
0.145	0.147	0.155	0.157
0.145	0.145	0.233	0.236
		0.078	0.078
		0.233	0.225
0.145	0.147	3.100	3.095

A blank must be run on the chromium determination, as a little bit of MnO_2 persists in solution and runs uniformly the same.

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A RAPID CONTROL METHOD FOR THE DETERMINATION OF OIL IN GRAINS.

By E. P. HARDING AND LILLIAN L. NYE.

Received July 30, 1912.

The solvents ordinarily used for determining extract

[1] THIS JOURNAL 4, 249.

matter, fats and oils in food-stuffs and the various industrial and commercial products are ether, petroleum ether, carbon tetrachloride, carbon bisulphide, acetone, chloroform and alcohol. Of these, pure anhydrous ether and low-boiling petroleum ether are most generally accepted for determining fats and oils. In cases of dispute and litigation, ether may be considered as the official solvent.

The principal objection to ether and petroleum ether as solvents in control work is the length of time given for complete extraction, the usual time being sixteen hours.[1] The extraction must also be made on a moisture-free sample. It is very difficult, almost impossible, with a common hot air oven not provided with a thermostat to obtain duplicate results on foods and food materials, especially the cereals. A slight variation of the temperature from 100° C.[2] affects not only the percentage of moisture but also as a consequence the percentage of oil in the dried sample.

The object of this paper was to find a suitable solvent and method that would extract the oil from grains completely in a comparatively short time when applied either to the oven-dried or the air-dried sample. Such a solvent was found to be carbon tetrachloride.

Carbon tetrachloride has been used by A. P. Bryant[3] for extracting oil from vegetable substances and from one meat sample. The results obtained agreed with those obtained with ether as a solvent. The extraction was made in a Knorr apparatus, the solvent distilled and the residue dried to constant weight at 100° C. The extraction required two hours and the final drying two hours. The last trace of carbon tetrachloride was, however, driven off with some difficulty and in some cases the drying was completed at 120° C. This method requires at least four hours, the long drying at 100° and the final drying at 120° may be considered as an objection to the method when applied to substances containing much unsaturated oil.

In the authors' method, the grain is extracted at the temperature of boiling carbon tetrachloride (about 76°), the mass cooled, mixed with absolute alcohol, water and petroleum ether, thoroughly shaken, whirled in a centrifuge, the oil blown off, filtered into a tared flask, and dried to constant weight in a casserole water bath. The time required for a complete determination is less than three hours.

The apparatus used is a thick-walled glass cylinder, $7^1/_2$ inches long and $1^1/_4$ inches in diameter, a water bath, a reflux condenser, a condensing tube, a centrifuge, a blow-off tube similar to that used with a Werner-Schmidt apparatus, a Soxhlet extractor provided with a glass stopcock connected to a reflux condenser, a receiver, a casserole five inches in diameter, a flask, $2^1/_2$ inches bottom diameter by 4 inches in height, and a small funnel.

The reagents used are distilled water, absolute alcohol, redistilled carbon tetrachloride, b. p. 76°, and distilled petroleum ether with a boiling point of 53°–68°.

In making a determination a burner is put under the water bath, the material weighed out from 1 to 3 grams (depending upon the amount of oil in the substance), transferred to the cylinder, 25 cc. of carbon tetrachloride added, the cylinder connected with the condenser and placed in the water bath where it is kept for one hour at the temperature of boiling CCl_4. In the meantime the flask is cleaned, rinsed successively with alcohol and petroleum ether and heated in the casserole bath to constant weight. In weighing the flask it is removed from the casserole, held under a tap of flowing water until cooled, then wiped with a dry towel and the weighing made within one minute's time.

At the end of one hour's boiling the cylinder is detached, attached to the condensing tube and 12.5 cc. of CCl_4 is distilled off into the receiver. The cylinder is then cooled by holding under the water tap, 25 cc. of absolute alcohol is added and the tube shaken: 12.5 cc. of water is added and the tube again shaken, then 50 cc. of petroleum ether is added and the whole thoroughly mixed by shaking. The cylinder is then put into a centrifuge and whirled for ten minutes at the rate of about 1000 revolutions per minute. The cylinder is taken out, the rubber stopper removed, the blow-off tube inserted and the petroleum ether layer blown off through a filter into the tared flask. The flask is then connected with the Soxhlet apparatus and the petroleum ether distilled off. In the meantime 5 cc. of CCl_4, 5 cc. of absolute alcohol and 50 cc. of petroleum ether are added to the cylinder, the whole thoroughly shaken and whirled for five minutes. The petroleum layer is then blown off through the filter into the flask. The flask is again connected with the Soxhlet apparatus and 5 cc. of CCl_4, 5 cc. of absolute alcohol and 50 cc. of petroleum ether is added to the cylinder which is whirled once more for five minutes. The petroleum ether layer is again blown off as before, the filter washed with petroleum ether, which is then removed by means of the Soxhlet apparatus. The flask is then put into the casserole water bath, which is boiling, and heated for fifteen minutes and weighed under the same conditions as the empty flask was weighed. It is heated again for fifteen minutes and weighed. This fifteen-minute period of heating and weighing is repeated until constant weight is obtained. Two heatings of fifteen-minute periods resulted in a constant weight.

In trying out the method each blow-off was blown into a separate flask, weighed separately in order to determine the proportionate amount of oil in each blow-off and the number of blow-offs necessary to remove all of the oil. Extractions were also made on the oven-dried sample with pure anhydrous ether and petroleum ether of a boiling point 53° to 68° in order to compare the results with those obtained with these solvents.

The following results were obtained on "Diamond

[1] Bur. of Chem., *Bull* **107**, 49 revised
[2] THIS JOURNAL, **2**, 19.
[3] *J. Am. Chem. Soc.*, **26**, 568.

Cut" corn meal, an approximately 2-gram sample being used in the extractions:

Percentages.

	Carbon tetrachloride.				Petroleum ether.	Ether.
	Dry sample.		Wet sample. (Cal. on dry.)		16 hours' extraction.	16 hours' extraction.
1st blow-off	2 91	2.93	3 03	3 02		
2nd blow-off	0 24	0 36	0 17	0 28		
3rd blow-off	0.05	0.00	0.07	0.00		
Total,	3 20	3 29	3 27	3 30	3 21	3 20	3 23	3 39

On millet flour from Crookston, Minn., containing 7 per cent. of moisture.

CARBON TETRACHLORIDE.

Percentages.

	Dry sample.			Wet sample. (Cal. on dry.)	
1st blow-off	4.26	4 30	4 20	4.42	4.37
2nd blow-off	0.27	0.14	0.32	0.34	0.18
3rd blow-off	0.02	0.09	0.00	0.00	0.12
Total,	4.55	4.53	4.52	4.76	4.76

PETROLEUM ETHER.

Percentages.

Dry sample.					
10 hours	4.56	6 hours longer	0.02	Total	4.58
10 hours	4.55	6 hours longer	0.02	Total	4.57
6 hours	4.46	24 hours longer	0.10	Total	4.56
6 hours	4.55	24 hours longer	0.01	Total	4.56
10 hours					4.60
16 hours					4.55

ETHER.

Percentages.

Dry sample.					
10 hours	4.62	6 hours longer	0.07	Total	4.66
10 hours	4.76	6 hours longer	0.02	Total	4.78
10 hours	4.61	18 hours longer	0.02	Total	4.63
10 hours	4.57	18 hours longer	0.03	Total	4.60
16 hours					4.62

On wheat germ from the Washburn Crosby Milling Co., Minneapolis.

CARBON TETRACHLORIDE.

Percentages.

	Dry sample.	Wet sample, No. 1 (Cal. on dry.) No. 1.	Av. of 7.	Different sample, No. 2. Dry sample.	Wet sample. (Cal. on dry.)
1st blow off	10 15	10 14	10.23	11.77	11 78
2nd blow off	0.51	0.54	0 47	11.90	11 90
3rd blow-off	0.15	0.17	0.11	11.78	11 77
4th blow-off	0.02	0.01	0.02		11.87
Total,	10.83	10.86	10.83		

PETROLEUM ETHER.

Sample No. 1. Percentages.

5 hours	10.78	5 hours longer	0 15	Total	10.93
5 hours	10.74	5 hours longer	0 20	Total	10.94
5 hours	10 74	5 hours longer	0 12	5 hours longer 0 07 Total	10.93
6 hours					10.92
6 hours					11.01
10 hours					10.95
10 hours					10.89
10 hours					11 09
16 hours					11.11
16 hours					11.00
16 hours					11 04
16 hours					11.01
16 hours					11 07

ETHER

Sample No. 1. Percentages.

5 hours	11 57	5 hours longer 0 16	Total 11.73
10 hours			11.67
10 hours			11 46
10 hours			11 45
10 hours			11.26
10 hours			11.35
16 hours			11.67
16 hours			11.48
16 hours			11 47
16 hours			11.61

The above method for the determination of oil in grains gives very satisfactory results compared with those obtained by means of petroleum ether and ether as solvents.

(1) It is a short method, two and one-half hours being required for a complete determination.

(2) There is no difficulty encountered in removing the last trace of the solvent.

(3) The oil extracted is purer than that extracted by petroleum ether or ethyl ether, as shown by a higher iodine absorption value.

(4) It is a rapid control method.

CHEMICAL LABORATORY,
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MINNEAPOLIS.

SOY BEAN CHEESE.[1]

By WILLIAM V. LINDER.

Received Aug. 22, 1912.

In the line of my official work a few weeks ago, I had occasion to examine two samples sent to the laboratory from a western state; these were suspected of being filled cheese. Cheese made from cream, or milk containing fat other than that derived from the cream or milk used in its production, is classed as filled cheese and subject to an internal revenue tax of one-quarter of a cent per pound.

The samples somewhat resembled in appearance and taste a very soft and mushy cream cheese, saturated with water.

On account of the difficulty of obtaining a true sample, due to the large amount of water present, it was decided to make an analysis on a moisture-free basis only. About 100 grams were dried in an electric oven and the analysis made on the dry sample, with the following results:

Laboratory No.	Protein. Per cent.	Fat. Per cent.	Ash. Per cent.	Sugar.
429991	39.31	7.80	2.36	None
43285	45.07	6.04	1.83	None

One hundred grams of each sample were extracted with ether and the fat obtained examined, with the following results:

Laboratory No.	Index of refraction at 25° C.	Iodine No.
42991	1.4749	130.4
43285	1.4742	128.7

From the results obtained it was clear that the fat could not have been derived from milk or cream and

[1] Published by permission of the Commissioner of Internal Revenue.

the failure to find milk sugar also indicated that no milk or cream had been used in their production.

The analysis of the fat indicated that it was soy bean oil, and as soy beans contain a large percentage of protein, it was at once suspected that this was one of the numerous products made from them. It is a well known fact that in China and Japan soy beans have been used for hundreds of years, not only to produce an edible oil, but in the production of many other food products.

Two hundred grams of soy bean meal, ground from the whole bean in the laboratory, were thoroughly mixed in 1000 cc. of cold water. After standing twelve hours fermentation set in and continued for three days. No effort was made to ascertain the nature of this fermentation. At the end of this time the mash, upon which a mold had started to grow, was strained through cheese cloth; a heavy, milky liquid was obtained. Numerous methods were tried to coagulate the suspended and dissolved protein, such as the addition of acids, rennet, and heat. Heating upon the steam bath seemed to give the most satisfactory results as the dissolved material coagulated and settled out upon standing.

The coagulated mass was filtered, giving a product that was identical in appearance, taste and odor with the two samples examined. The dried product was analyzed showing the similarity beyond any doubt.

Laboratory No.	Proteins. Per cent	Fat. Per cent.	Ash. Per cent	Sugar.
44288	59.46	11.86	5.19	None

The investigation proved that the product submitted for examination could not be classed as filled cheese, although a very good substitute. Cheese prepared from soy beans must be consumed within a few days as it deteriorates very rapidly.

While making this investigation I confirmed the work of J. Ruhiah,[1] who found sucrose present in soy beans. The beans that I used contained 4.4 per cent. sucrose.

As thousands of tons of soy beans are used annually in making oil, it does not seem improbable that a method could be found which would make the recovery of the sucrose possible without reducing the yield or injuring the quality of the meal for feeding purposes. It would be a source of profit from an industrial product that is now entirely wasted.

LABORATORY BUREAU OF INTERNAL REVENUE,
WASHINGTON, D. C.

LABORATORY AND PLANT

A NEW FORM OF ORSAT APPARATUS.

By L. M. DENNIS.

Received October 14, 1912.

In the analysis of commercial grades of sodium carbonate there early arose a demand for a rapid and convenient method for the determination of carbon dioxide, which was met in 1868 by the apparatus designed by Schlösing and Rolland.[1] In 1874 Orsat patented a device[2] that was based directly upon the principle of the apparatus of Schlösing and Rolland, and that attracted considerable attention at the time and rapidly came into general use. Because of its compactness and ease of manipulation, the Orsat apparatus has been and still is very generally employed by gas analysts. In its original form, however, and even in some of the later modifications, it possesses certain inherent faults, and the unsatisfactory character of the analytical results that are obtainable with the various forms is evidenced by the large number of changes in its construction that are constantly being brought forward in chemical journals. The chief objection to the apparatus is the incompleteness of the absorption of such gases as oxygen and carbon monoxide. The researches of Gautier and Clausmann, Bendemann, Hankus, Hempel, Nowicki, Hahn, Dennis and Edgar, and others, have demonstrated that the complete removal of oxygen by alkaline pyrogallol and of carbon monoxide by cuprous chloride can be effected only when the absorbent and the gas are shaken together, or when the gas is, in some manner, brought into prolonged and intimate contact with the absorbent. With most of the suggested forms of the Orsat absorption pipette, the removal of oxygen and carbon monoxide is quite incomplete unless the gas is allowed to stand in contact with the absorbent for a very considerable length of time, or is passed back and forth many times between the burette and pipette. Failure to recognize this inadequacy of the apparatus frequently results in the incomplete removal of oxygen, and, as a consequence, a decrease in volume is observed when the gas mixture is next passed into the cuprous chloride pipette. In very many cases the analyst has, in this manner, been led into reporting carbon monoxide in a gas mixture, such as flue gas, when in fact no carbon monoxide is present, the decrease in volume being due solely to the absorption, by cuprous chloride, of oxygen that still remains in the gas mixture.

In recent years several interesting and some valuable suggestions for increasing the completeness and rapidity of absorption in the Orsat apparatus have appeared in chemical journals. Bendemann proposes[2] that two pipettes be used for the absorption of oxygen by alkaline pyrogallol and two for the removal of carbon monoxide by cuprous chloride. This would undoubtedly lessen the errors of the determinations but would hardly remove them entirely. More worthy of consideration are the proposed modifications of the form of the absorption pipette to bring

[1] *Annales de chimie et de physique*, 4 serie, **14**, 55 (1868); *Chem. News*, **29**, 176 (1874).

[1] See *Chemical Abstracts*, **4**, 1789, 1912.

[2] *J. f. Gasbeleuchtung*, **49**, 853 (1906).

gas and liquid into intimate contact. Mos of these are based upon the construction described in 1899 by E. Hankus[1] and shown in Fig. 1. The gas enters the

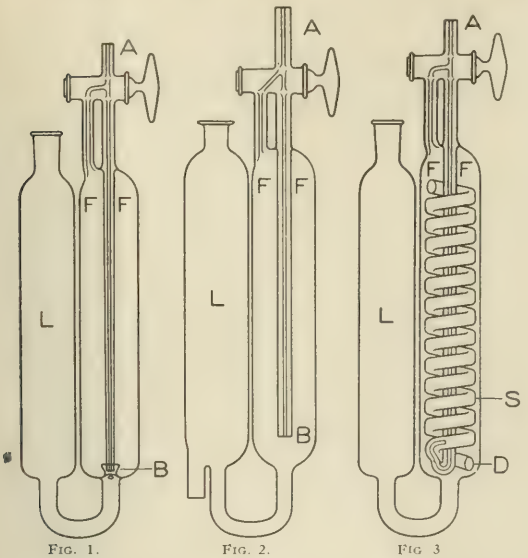

Fig. 1. Fig. 2. Fig 3

pipette through *A*, passes downward through the capillary and, by impinging on the plate *B*, is broken up into minute bubbles which then pass upward through the absorbing liquid. The gas is brought back into the burette by turning the stopcock through an angle of 180° and lowering the level bottle of the burette.

In 1911 the Chemists' Committee of the United States Steel Corporation described[2] and *copyrighted* drawings of an absorption pipette (Fig. 2) that is quite similar to the form proposed twelve years earlier by Hankus, but is slightly less efficient than the Hankus pipette (see results below) since it permits the gas to escape freely in large bubbles from the lower end of the capillary tube.

The pipette devised by Nowicki[3] and improved by Heinz[4] (Fig. 3) yields more complete absorption than that of Hankus. The gas passes downward through the straight capillary tube *A* and then rises in small bubbles through the spiral tube *S*, which insures long and thorough contact between the gas and absorbent. A short tube, *D*, is attached to the lower end of the spiral, and fresh absorbing liquid is drawn upward through this opening when the gas bubbles rise through the spiral. Experience has shown, however, that when this form of absorption pipette is used for the determination of oxygen with alkaline pyrogallol, the gas is frequently trapped in the spiral. Moreover, the pipette is so fragile that it is often broken in transportation, which renders it unsuitable for use in a portable apparatus.

The very rapid and complete absorption of gases that, upon experiment, was found to be obtainable with the Friedrichs Gas Washing Bottle,[1] led the writer to employ the same principle in the construction of an absorption pipette for the Orsat apparatus, the form of pipette that was finally adopted being that shown in Fig. 4. The gas mixture enters the pipette

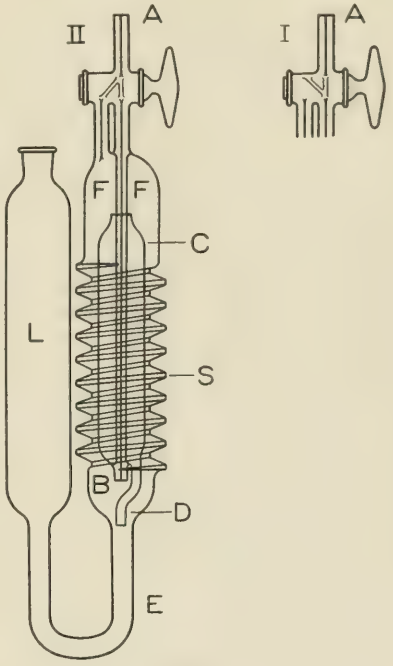

Fig. 4.

through the capillary *A* (the stopcock being in position I), and, passing downward through the capillary, escapes at *B*. It then rises, and in so doing follows the spiral *S*. The rising gas carries some of the absorbing liquid with it, and this liquid then flows down on the inside of the cylinder *C* and mixes with the main body of the absorbent again at *D*. After the gas has risen through the spiral and has collected in the space *F*, the stopcock is turned through 180° to position II and the gas is then drawn back into the burette.

An experimental comparison of the different forms of Orsat pipette here illustrated has been made by Mr. F. H. Rhodes. In the first series of comparative determinations, oxygen in atmospheric air was absorbed by means of an alkaline solution of pyrogallol. The absorbent was prepared by dissolving one part by weight of pyrogallol in three parts by weight of water and adding one volume of this solution to four volumes of a solution of potassium hydroxide prepared by dissolving one and one-half parts by weight of potassium hydroxide in one part by weight of water. One hundred cc. of air were measured off in a Hempel burette, and this was then connected with the pipette under examination, and the gas sam-

[1] *Oesterr. Chem. Ztg.*, **47**, 81 (1899); *J. Gasbeleuchtung*, **49**, 367 (1906).
[2] *Met. and Chem. Eng.*, **9**, 303 (1911).
[3] *Oesterr. Zeit. f. Berg. Hütt.*, **53**, 337 (1905).
[4] *J. f. Gasbeleuchtung*, **49**, 367 (1906).

[1] *Z. anal. Chem.*, **50**, 175 (1911).

ple was passed back and forth between the absorption pipette and the burette until all of the oxygen in the sample had been absorbed. The air was passed into the several pipettes at a uniform speed. The absorption pipettes that were tested were:

(*a*) The usual form of Orsat pipette, which is filled with glass tubes to increase the absorbing surface;

(*b*) The Hankus pipette (Fig. 1);

(*c*) The absorption pipette recommended by the Chemists' Committee of the United States Steel Corporation (Fig. 2);

(*d*) The Nowicki-Heinz spiral absorption pipette (Fig. 3); and

(*e*) The new form of pipette here described (Fig. 4).

The sample of air was passed over into each absorption pipette in one minute. It was then immediately drawn back into the burette and again passed into the absorption pipette at the same speed as before. This was continued until all of the oxygen was absorbed. The results given in the tables are the averages of numerous determinations.

TABLE I.

Time (minutes).	(*a*) Orsat usual form.	(*b*) Hankus pipette.	(*c*) U. S. steel committee.	(*d*) Nowicki-Heinz pipette.	(*e*) Pipette new form.
1	8.0	11.2	9.0	20.6	18.6
2	13.3	16.5	14.2	20.8	20.4
3	16.7	19.1	17.2	20.9	20.9
4	18.7	20.1	18.8		
5	19.5	20.5	19.8		
6	20.2	20.7	20.2		
7	20.4	20.8	20.6		
8	20.8	20.9	20.9		
9	20.9				

In the analyses here tabulated, the sample of air was first passed into each pipette in two minutes, that is, at half the earlier speed. It was then immediately drawn back into the burette and passed a second time into the pipette in one minute.

TABLE II.

Time (minutes).	(*a*) Orsat usual form.	(*b*) Hankus pipette.	(*c*) U. S. steel committee.	(*d*) Nowicki-Heinz pipette.	(*e*) Pipette new form.
2	10.3	15.6	12.3	20.7	20.6
1 minute more	17.2	18.3	17.2	20.9	20.9

The above results render it evident that the complete absorption of oxygen from air can be effected with the first three forms of pipette only by repeated passage of the gas sample into the pipette and back into the burette. The Nowicki-Heinz pipette and the spiral pipette here proposed seem to be of nearly equal efficiency, but the former is open to the objections already noted.

To ascertain the efficiency of the new spiral pipette in the absorption of carbon monoxide, mixtures of this gas with known amounts of air were prepared; oxygen was determined in one spiral pipette by absorption with an alkaline solution of pyrogallol and carbon monoxide in a second spiral pipette by absorption with an ammoniacal solution of cuprous chloride. In the absorption of oxygen the gas mixture was passed into the pipette in two minutes, was drawn back, and then passed in a second time in one minute. In the absorption of carbon monoxide the same time intervals were found to give complete absorption of the gas unless the amount of carbon monoxide exceeded 25 per cent. In such case it was found necessary to pass the gas mixture three times into the pipette, the first time in two minutes, and the second and third times in one minute each. The results were as follows:

TABLE III.

		I.	II.	III.
Oxygen.....	Taken	17.7	16.2	13.2
	Found	17.8	16.3	13.2
Carbon monoxide..	Taken	15.8	22.9	37.3
	Found	15.8	22.8	37.4

It thus appears that with this form of absorption pipette both oxygen and carbon monoxide can be removed as completely and as rapidly as is possible with the Hempel absorption pipette in which the gas and absorbent are shaken together.

A further error in analyses made with the usual forms of the Orsat apparatus results from the incorrect position of the measuring burette.[1] After the removal of the absorbable constituents of the gas mixture, the capillary tube that connects the burette with the pipettes remains filled with the combustible residue; consequently, when a portion of this residue is measured off in the burette and is passed to the combustion apparatus through the capillary tube above the pipettes, it will carry with it the combustible gas remaining in that capillary. This difficulty may be avoided by filling the connecting capillary with the confining liquid (water) in the manner suggested by Pfeifer,[2] or more simply by placing the burette between the absorption pipettes and the combustion apparatus in the manner recommended by Hahn.[3]

Since the Orsat apparatus is chiefly employed for the determination by absorption in liquid reagents of carbon dioxide, oxygen, and carbon monoxide, it is, in the opinion of the writer, preferable to limit the apparatus to the determination of these three gases and to construct it in such manner as to render it easily possible to connect the burette when so desired with suitable special apparatus for the determination of hydrogen and hydrocarbons. The apparatus is thus rendered smaller, more easily portable, and less fragile, and the combustion results, with proper apparatus, will usually be much more accurate than with the imperfect devices contained in the many forms of the Orsat apparatus now upon the market.

A further drawback in the usual forms of Orsat apparatus is to be found in the rubber bulbs that are attached to the level cylinders of the pipettes to protect the various reagents from the air. These bulbs rapidly deteriorate, and after short use fail to accomplish the purpose for which they are intended.

In the hope of remedying some, if not all, of the de-

[1] See Hahn, *Zeit. d. Vereins deutscher Ingenieure*, **1906**; *J. f. Gasbeleuchtung*, **49**, 367 (1906).

[2] *J. f. Gasbeleuchtung*, **51**, 523 (1908).

[3] *Loc. cit.*

fects of the Orsat apparatus that have been enumerated above, the writer has designed the modification shown in Fig. 5.[1]

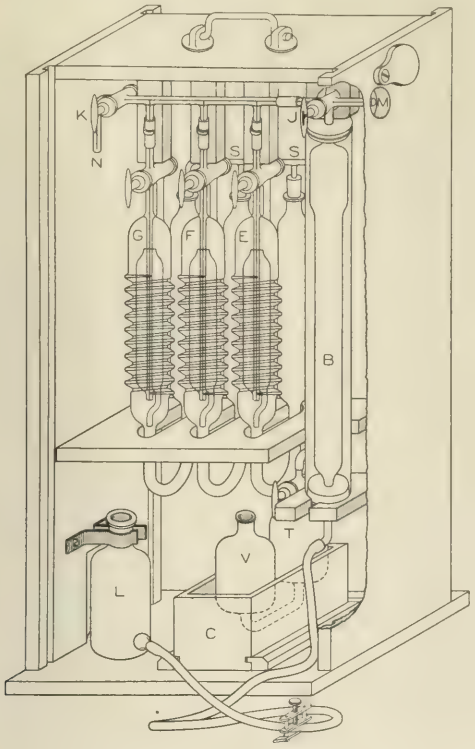

FIG. 5.

The burette *B* has a capacity of somewhat more than 100 cc. and is graduated from a point near the bottom upward to the stopcock *J*. The stopcock is a three-way stopcock, the position of which is shown by means of a black glass ⊣ fused to its outer surface. The capillary tube connecting *J* with the pipettes and with the stopcock *K* has an external diameter of 7 mm. and an internal diameter of 1 mm. In fusing on the branch capillaries that extend downward to the three pipettes, the internal diameter of the capillary should, at no point, be much greater than 1 mm. if the apparatus is properly made. The three absorption pipettes, *E*, *F* and *G*, are of the form already described, and are filled, respectively, with solutions of potassium hydroxide, alkaline pyrogallol, and ammoniacal cuprous chloride. They are connected with the capillary tube from the burette by means of pieces of soft, black rubber tubing of 1.5 mm. thickness of wall, and these rubber tubes are held in place by wire hooks that pass through the blocks behind the joints, and have threaded ends upon which small set screws are placed. This method of attachment renders it easily possible to remove all the glass parts from the frame. Into the open ends of the three level tubes of the pipettes are inserted one-hole rubber stoppers, and through the openings of these stoppers pass the branch tubes from the tube *SS*, that is 7 mm. external diameter and 1 mm. thickness of wall. This tube passes downward and is joined by a piece of rubber tubing to the upper side of the stopcock attached to the cylindrical vessel *T*, which in turn is connected with *V* by the glass tube shown by the dotted line. After the pipettes have been filled with the several reagents, the stoppers connecting the level tubes with the tube *SS* are inserted in place and the protecting reservoir *VT* is half filled with water. As the gas is driven over from the burette into the pipette and is drawn back into the burette, the water in *VT* rises and falls, but protects the reagents at all times from contact with the air. The level bottle *L* is held in place by a clamp when the apparatus is in transport.

After the absorbable gases have been removed from the gas mixture, the combustible residue may be burned, if so desired, by connecting the capillary *M*, which has an external diameter of 6 mm. and a bore of 1 mm., with a combustion pipette or other suitable device. The case containing the apparatus is 57 cm. high, 27 cm. wide and 16 cm. deep. The panels forming the front and back of the case are removed when the apparatus is in use. As illustrative of the speed, accuracy, and uniformity of the results yielded by this apparatus, the following analyses of a mixture of carbon dioxide, oxygen, and carbon monoxide may be cited. A single passage of the gas mixture in one minute into the first absorption pipette serves to completely remove the carbon dioxide. In the determination of oxygen and carbon monoxide each gas was twice passed into the absorption pipette, the first time in two minutes, the second time in one minute.

TABLE IV.

	I.	II.	III.	IV.
Carbon dioxide, per cent.	3.1	3.1	3.2	3.1
Oxygen, per cent.	6.0	6.0	5.9	5.9
Carbon monoxide, per cent.	22.5	22.6	22.6	22.7

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ITHACA, N. Y.

[1] The apparatus is manufactured by Greiner and Friedrichs, Stützerbach in Thüringen, Germany

THE STORMER VISCOSIMETER AND THE VALUE OF VISCOSITY DETERMINATIONS BY ITS USE.

By GILBERT RIGG AND J. L. CARPENTER.

Received Oct. 9, 1912.

The Stormer viscosimeter is the instrument proposed for use in bringing paints to a common viscosity, and for the comparison of the viscosities of different paints. It may be briefly described as follows: A weight attached to a string falls vertically from the instrument. The string pays out over a vertical pulley as the weight falls, and unwinds from about the shaft of a large toothed wheel, this wheel lying in a horizontal plane. The large wheel fits into a small gear on the shaft of the viscosimeter cylinder. When the large wheel is caused to revolve by the falling weight, this shaft is turned, and the cylinder attached to its lower end is revolved in whatever liquid

there is in the cup below. A screw gear at the top of this shaft fits into the teeth of an indicator wheel, and the whole instrument is so geared that a complete revolution of the indicator wheel represents 100 turns of the cylinder in the cup below. A small water bath surrounds the container cup, and rough temperature control may thus be maintained.

The directions for using the instrument are substantially as follows: Take the time for 100 revolutions in water as unity. Then the relative viscosity of another fluid will be the time required for 100 revolutions divided by the time for 100 revolutions in water. If a liquid is found too viscous for comparison with water, first determine the viscosity of an intermediate liquid, increase the weight and then use the intermediate liquid as standard. After this, calculate back to water as unity.

Assuming that in many cases the instrument would be accepted as quite accurate, and that the instructions for its use would be considered complete, an investigation of its merits was determined upon.

In the directions accompanying the instrument, the very important factor of friction in the machine seems to have been overlooked, and this has an important influence upon the values obtained for viscosities. This is especially noteworthy, when it is necessary to use an intermediate liquid, and therefore increase the falling weight.

The following table shows the necessity of determining the friction factor with each change of weight, as well as the necessity for introducing a correction for the instrument's friction into each relative viscosity value.

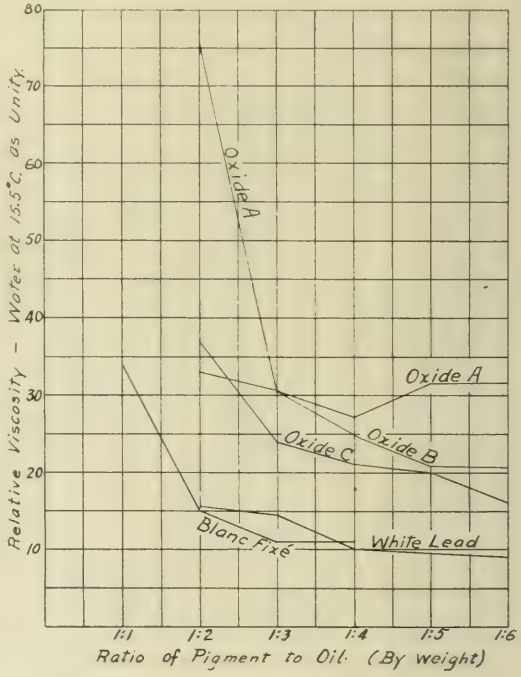
In the table, the columns represent the following: (1), the mass in grams of the falling weight; (2), the time in seconds for the viscosimeter cylinder to revolve 100 times in the empty cup below—the value in air, which represents the retardation of the machine, due to its own friction; (3), time in seconds for cylinder to revolve 100 times in water at 15.5° C.; (4), time for 100 revolutions in linseed oil at 15.5° C.; (5), ratio of viscosities of water and oil uncorrected, *i. e.*, using the values in columns (3) and (4) without regard to the friction correction in column (2); (6), time in seconds for 100 revolutions of cylinder in water after correction for friction, as per column (2); (7), time for 100 revolutions in oil corrected for friction in (2); (8), corrected relative viscosities of water and oil, *i. e.*, ratio between values shown in (6) and (7).

Taking water as unity, columns (5) and (8) show the effect that the friction factor exerts on the relative viscosities of two liquids. Not to use the friction factor is similar in effect to a failure to weigh a crucible before a moisture determination.

The ratio between the viscosities of two liquids will be referred to hereafter in this paper as "uncorrected" or "corrected," depending upon whether the friction value of the machine has been taken into account or not, "uncorrected" meaning that the ratio is between the *observed* times for 100 revolutions of the wheel and "corrected" meaning that the ratio is between the corrected times for each liquid—the corrected time being the observed time minus the time for the cylinder to revolve 100 times in air.

The following tables and curves show the relative viscosities of several pigments in different quantities of oil, a constant weight on the turning wheel being used throughout.

The relative viscosity values are expressed in terms of water as unity, and the ratios of pigment to oil are shown in the top horizontal column.



As is clear, upon inspection of the tables, there occur wide variations between the corrected and uncorrected values. And it follows from this, that any dust or rust accumulating in any of the bearings or gears of the machine, modifying the friction correction, would change the relative viscosity values if the correction were not considered.

The above experiments were carried out with a three-fold purpose in view: *First*, to determine the rate of change of fluidity of the several pigments in oil upon addition of more oil; *Second*, to determine and compare the relative viscosities of the several pigments in equal quantities of oil; *Third*, to find out the effect of the friction of the instrument upon the relative viscosities.

A series of experiments was next carried through to determine the effect of changing the mass of the falling weight which drives the cylinder in the viscosimeter cup. The instrument was carefully cleaned and oiled, and new friction constants determined with the

TABLE I.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
	sec.	sec.	min.	sec	Ratio.	sec.	min. sec.	Ratio.
38.42	6.4	13.6	1	14.9	1.5.5	7.2	1 8.5	1.9.5
51.00	5.0	9.7		49.7	1.5.1	4.7	44.7	1.9.5
73.84	3.2	6.6		30.4	1:4.6	3.4	27.2	1:8

TABLE II. OXIDE "A" AND P. M. P. OIL.

Ratio oxide to oil by weight.	1:2	1:3	1:4	1:5	1:6
Uncorrected viscosity.....	39.9	14.4	12.8	15.0	15.0
Corrected viscosity...	76.2	31.2	27.5	32.0	32.0

TABLE III. OXIDE "B" AND P. M. P. OIL.

Ratio oxide to oil by weight.	1:2	1:3	1:4	1:5	1:6
Uncorrected viscosity ...	17.4	14.4	11.8	10.0	10.0
Corrected viscosity...	32.9	31.2	25.2	21.2	21.2

TABLE IV. OXIDE "C" AND P. M. P. OIL.

Ratio oxide to oil by weight.	1:2	1:3	1:4	1:5	1:6
Uncorrected viscosity.....	19.7	11.6	10.2	9.6	8.7
Corrected viscosity.....	37.3	25.0	21.7	20.2	18.2

TABLE V. EAGLE WHITE LEAD AND P. M. P. OIL.

Ratio pigment to oil by weight.....	1:2	1:3	1:4	1:5	1:6
Uncorrected viscosity.....	8.6	8.1	6.0	5.7	5.5
Corrected viscosity.....	15.7	14.7	10.7	10.1	9.7

TABLE VI. BLANC FIXE ($BaSO_4$) AND P. M. P. OIL.

Ratio pigment to oil by weight.....	1:1	1:2	1:3	1:4
Uncorrected viscosity.....	18.2	8.0	6.5	6.1
Corrected viscosity.....	34.4	14.5	11.7	10.8

various weights to be used; these operations in fact were carried through at the beginning of each day. Three different weights were used, and the constants for all the liquids tested were determined with these three weights without removing the liquid from the cup. This rendered it absolutely certain that the same sample of liquid was tested by the use of three different weights.

The following table shows the results:

TABLE VII.

	Seconds for 100 revolutions of cylinder—in						Relative viscosities—water unity.			
Driving weight.	Water		Oil		Paint		Oil		Paint	
Grams.	Air.	Obs.	Cor.	Obs.	Cor.	Obs.	Cor.	Uncor.	Cor.	Uncor.	Cor.
38.42	4.8	10.2	5.4	64	59.2	600	595.2	6.27	11.1	58.9	110.2
51.00	3.8	7.8	4.0	47	43.2	243	239.2	6.03	10.8	31.2	59.8
73.84	2.8	5.8	3.0	30	27.2	111	108.2	5.18	9.1	19.1	36.1
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)

It is quite obvious that a liquid such as an oil cannot undergo a change of viscosity 11.1 to 9.1, column (10), or a paint undergo a change from 110.2 to 36.1, column (12), in a few minutes time—while it is neither removed from the cup nor suffers a change of temperature of more than 2 or 3 degrees. The radical variations shown in the relative viscosity values with changing driving weight on the cylinder, as shown in columns (10) and (12), at once make it clear that in order to secure comparable figures in the ratio of time for 100 revolutions of the cylinder in different liquids, a constant weight must be used.

Another error, likely to be sustained, is uncovered if the directions for using an "intermediate" liquid are critically tried out. Quoting again from the directions for use accompanying the instrument, the following paragraph appears: "If a liquid of medium viscosity, say 6, is used as an intermediate to determine the viscosity of a very viscid fluid, then the time for the unknown must be divided by the time for the known and this result multiplied by the figure of the fluid used (in this case 6) to obtain the viscosity with reference to water, which is the standard or unity." Without doubt this recommendation is meant to facilitate work when a change in the mass of the driving weight is made, and in the case that the weight is so heavy that it causes the cylinder to revolve very rapidly in the standard liquid—water—thereby rendering errors more liable in the reading of the rapidly turning indicator wheel.

Taking the recommendation at its face value, which indeed seems theoretically faultless, and applying it to a case in the above table where the water figure was actually determined, we obtain the following results: In columns (9) and (10) the uncorrected and corrected values of oil are 6.27 and 11.1, respectively, for a driving weight of 38.42 grams. This we shall call the "intermediate" liquid. Now with a driving weight of 73.84 grams the time in seconds for 100 revolutions of the cylinder in the same oil was 30.0 (uncor.) and 27.2 (cor.), columns (5) and (6), and for a paint under the same conditions the time was 111.0 (uncor.), 108.3 (cor.), columns (7) and (8). Taking the uncorrected values and following the procedure given in the directions, we have $111/30 = 3.7$; 3.7×6.27 (figure of intermediate liquid) $= 23.20$, which is the calculated uncorrected viscosity of the paint. By actual comparison with water, the figure is 19.1. Thus we have $23.2 - 19.1 = 4.1$ or about 20 per cent. error. Again taking the corrected values: $108.2/27.2 = 3.98$; 3.98×11.1 (figure for intermediate liquid) $= 44.18$, which is the calculated corrected value for the paint. As actually determined (column 12) the value is 36.1. Now, $44.18 - 36.1 = 8.08$, or about 22 per cent. error.

These results raise a serious question as to the value of the instrument except within very narrow limits. It appears to be unsafe to use it other than for mere comparisons between liquids whose difference in fluidity will not require a change in the driving weight.

PALMERTON, PA.

APPARATUS AND METHOD FOR "CARBON TEST AND ASH RESIDUE" IN PETROLEUM LUBRICATING OILS.[1]

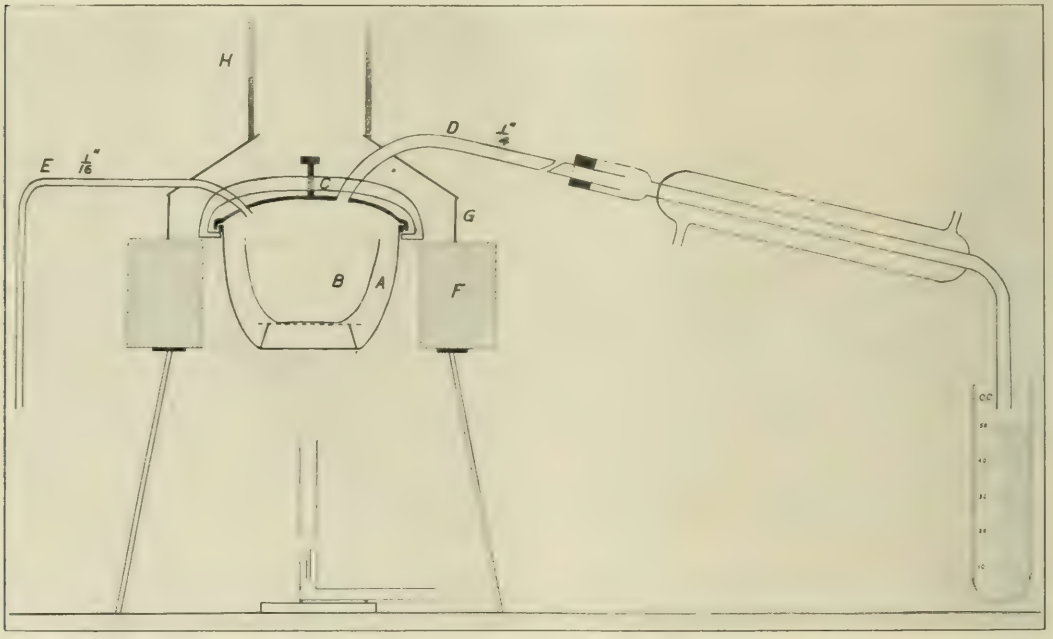
By P. H. CONRADSON.

In the examination of lubricating oils, especially those intended for gas and oil engines, air compressors, steam turbines, valve and cylinder oils, etc., the writer has found that the carbon residue from the so-called "Carbon test" sometimes contains other materials than carbon, such as chemicals from imperfect refining treatment, which would be considered as carbon unless further examined.

The following method and apparatus as shown in the accompanying photograph have proven satisfactory in most cases.

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

The apparatus consists of an iron crucible or retort (A Skudmore's Normal School or similar) of about 200 cc. capacity. Approximate inside dimensions; diameter on top 80 mm. ($3^1/_8$"), bottom 45 mm. ($1^3/_4$"), height 55 mm. ($2^1/_4$"). Inside of the crucible is placed upon a suitable support either a glass crystallizing dish, *B*, about 65 mm. ($2^1/_2$") in diameter or a platinum dish about 70 to 80 cc. capacity; the latter is preferred for further study of the carbon residue. In the lid of the crucible or retort is attached an exit or delivery pipe, *D*, 7 to 8 mm. ($^1/_4$") in diameter, bent as shown in the cut, and if so desired attached to a condenser; another pipe, *E*, with small bore 2 mm. ($^1/_{16}$") in diameter, the object of which is to blow out the heavy fumes generally produced, at the end of the distillation process



The test is conducted as follows: 35 grams of the oil are put in the weighed dish, which is placed in the iron retort or crucible, the cover *C* with its pipe connections being securely clamped down (an asbestos washer is found suitable to make a tight joint).

The apparatus, thus ready, is put on an asbestos block resting on a tripod and covered as indicated in the photograph with a sheet iron or asbestos hood, *G*, and on top of this a clay chimney, *H*, so as to distribute the heat uniformly during the process. To get the upper part of the apparatus hot at the beginning, a large gas flame is used for a few minutes and then lowered; the distillation should be uniform and at the rate of 1 cc. per minute. The long exit pipe should be kept comparatively cool with water-soaked waste in case a condenser is not used. At the end of the distillation, the flame is raised gradually to make the bottom and lower part of the apparatus red hot for at least when heavy fire test oils such as cylinder oils are tested, and at the last CO_2 or any other suitable gas is momentarily blown through the inlet pipe to drive out the heavy, dense fumes or vapors.

After cooling, the dish containing the carbonaceous residue is weighed, the latter ground fine and leached out first by boiling with water (water solution is tested with litmus paper for alkalinity and a few drops with silver nitrate solution for chlorids), next digested and boiled with dilute hydrochloric acid (1 + 1), filtered, washed, dried, and weighed again. The difference in weight, if any, gives approximately the amount of foreign matter in carbon residue. The carbon residue transferred back to the platinum dish is carefully burned off with a little pure nitrate of ammonia; if any residue is left, it is weighed, deducted from the first carbon weight and dissolved in hydrochloric acid.

The water and hydrochloric acid solutions are united and examined qualitatively or quantitatively, as the case may require, for impurities such as iron, alumina, lime, sulphuric acid and soda. (Some petroleum lubricating oils are compounded with lead, aluminum, zinc, lime or magnesium oleates, held either in solution or suspension, or both; before making the above test it is well to ascertain first if any of these compounds are present.)

	Carbon residue. Per cent.	Impurities in carbon residue. Per cent.
Turbine oil	0.02	None
1 Gas engine oil	0.83	0.126 Na_2SO_4
2 Gas engine oil	0.71	0.105 Na_2SO_4
3 Air compressor oil	0.66	0.092 Na_2SO_4
4 Motor oil	0.78	0.059 Na_2SO_4

Sulphur determination in No. 1 gas engine oil gave, according to Conradson's method:

In products of combustion (lamp) 0.08 per cent sulphur.

In wick from the oil (0.074 per cent. SO_3) 0.131 per cent. Na_2SO_4.

GALENA SIGNAL OIL COMPANY.
FRANKLIN, PA.

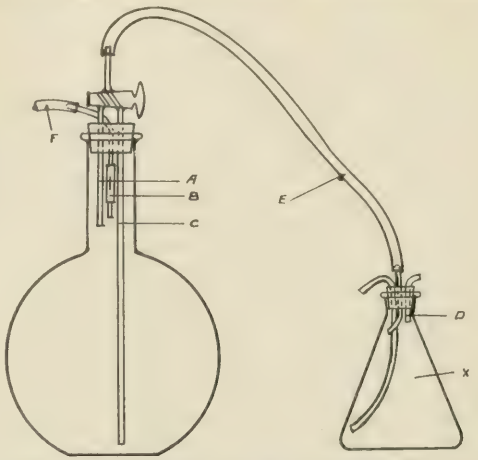
A SELF-FILLING MEASURING WASH BOTTLE.

By O. C. SMITH.

Received July 17, 1912.

If one wishes to wash a precipitate or residue with a certain volume of liquid, this apparatus is very convenient. By using a small necked flask for the smaller one, this arrangement will discharge to within a couple of drops of a given amount. In fact this apparatus will fill a 100 cc. flask to within one drop by exercising a little care.

The large flask is placed on the back of the desk out of the way. The rubber tube F is used to supply air. This ends in a tube, B, in which there is a slit to serve as a valve. By blowing in F water is forced through C and E into X and when this is full, out through D. By moving D the capacity of the flask can be changed. The stopcock is now turned and air enters through A and E into X. By closing D with



AUTOMATIC SELF FILLING MEASURING WASH BOTTLE

the thumb X is converted into an ordinary wash-bottle.

MISSOURI AGRICULTURAL EXPERIMENT STATION.
COLUMBIA

ADDRESSES

A PLAN FOR ORGANIZED RESEARCH AND ANALYTICAL CHEMISTRY IN SUCCESSFUL CHEMICAL MANUFACTURING.[1]

By WILLIAM C. FERGUSON.

INTRODUCTORY.

The constant growth in efficiency in Manufacturing Chemistry is largely the result of organization that insures the orderly use of every varied talent required; and occupying a very important place in such organization is the fullest use of a research staff and of analytical chemistry.

When it is realized that these departments should investigate all new processes, constantly improve existing ones, correct and explain irregularities of current operations, invent new processes; that they should determine the valuation and exact composition of all raw materials and finished products, the fixing of yields, the necessary control of different stages of many processes, etc., etc., it becomes clear that if these constructive forces are to be used to the fullest it must be through the creation of an organization that will automatically cause every department in the organization to coöperate with the Research and Analytical branches.

The methods to be described for accomplishing this are the result of the writer's experience for many years in charge of the research work of one of the largest chemical works in America, with many plants in different localities, and also in charge of the research work of the largest electrolytic copper refinery in America.

RESEARCH DEPARTMENT.

This department should investigate irregularities in current manufacturing; seek constantly to improve existing methods, and carefully consider new methods of promise as they arise.

Its duties should comprise: Investigating cheaper raw materials, new uses for products manufactured, new products, increased yields, greater purity of products manufactured, utilization of wastes, more efficient structural material, apparatus, etc., etc.

Great care should be exercised in the selection of the research staff which should embody all the varied talent and knowledge required in a wide field, and it is imperative here that only the very fit be retained as the achievements of this department will largely depend upon two factors—a highly efficient staff, and an organization that will invite, from every other department of the corporation, an automatic presentation of all questions requiring investigation.

The collective talent of this department should embrace thorough scientific education, especially in the principles of physics and chemistry; the power to imagine new processes, or causes of various irregularities of current manufacturing, combined with the ability to submit such ideas to the test of experimental proof; the habit of accurate observation and the skill to deduce from such observation the correct conclusion; and the quality of seeing right through all the unessentials to the one vital thing that counts. All of these qualities, diligently applied, together with a knowledge of manufacturing that will make all conform to practical conditions, are essential.

The department should have a manager with office organization and a properly equipped research laboratory with furnaces, filter presses, etc., where work can be carried on from a test tube scale to manufac-

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

turing in a large enough way to test practical difficulties and costs. There should be a Research Committee composed of the ablest technical minds of the organization, meeting regularly to consider and advise upon all important investigations.

Many questions presented to this department would be settled in debate negatively, but if experimental work be decided upon then, if the subject is new, the journal and patent literature bearing upon it should be abstracted and experiments usually begun upon a very small scale, increasing in size as warranted.

Each investigation should be made by a man selected on account of particular fitness and this man made responsible, but he should consult right along with other members of the staff whose knowledge or skill would be helpful, and progress made and difficulties encountered should be presented to the Research Committee at its regular meetings so that it could advise when necessary. At the conclusion of each investigation a detailed report should be made to the department. Exact estimate of cost should be made of each investigation in order to know the profit or loss in each particular case and also to estimate the value of the department as a whole.

The organization of this department should include:

(1) Systematic abstracting from the principal foreign and American journals and patents of all subjects of interest to the corporation; copies of these abstracts should go weekly to all who can use them, with instructions to study them carefully and to immediately advise the department of any subjects that seem to warrant investigation.

(2) Thorough abstracting from the literature in the case of new work undertaken, thus becoming familiar with all that has been published relating to the subject. Repetition of the work of others is thus saved, valuable suggestions received, and general knowledge of the subject enlarged.

(3) Systematic information should be constantly and promptly obtained of all records of imports and exports and duties on all finished products and raw materials that would interest the corporation in connection with its current business or as suggesting new articles of manufacture.

(4) Pamphlets describing machinery, structural material, etc., are many years in advance of books upon identical subjects. A pamphlet library should be maintained in coöperation with the engineering department.

All of the above work of translating, abstracting, etc., should be in charge of one competent man, with assistants if necessary.

(5) The superintendent should make monthly reports for the Research department embodying all ideas of their own or their assistants that might in any way warrant investigation. There is no doubt that valuable suggestions would be made through such a system thoroughly carried out that might otherwise be lost, and also that the plan would stimulate closer thought and observation concerning all the details in manufacturing.

(6) Members of the Research staff should visit all possible outside manufacturing plants with the object of acquiring knowledge that could be applied by the corporation to its own processes or organization.

(7) There should be, through proper connections, systematic prompt advices of all improvements in European practice that would be of value to the corporation.

(8) Salesmen should seek to understand the different processes and the various ways in which the company's products are used and also know what substitutes are used for the company's products and such information should be reported to the Research Department by the Sales Department as deemed necessary.

(9) Certain research work might be undertaken by candidates for the degree of Ph.D. in universities, thus making these institutions of learning take a coöperative part in developing practical questions being considered by manufacturers. This can be done and the work be as strictly scientific as in the case of pure research and will also place certain students in contact with possible future employers.

ANALYTICAL DEPARTMENT.

The Analytical Department, under the Chief Analytical Chemist, should control all work relating to sampling and analysis. So much depends upon prompt and accurate analyses that this department should occupy a high place in a rational organization. Its duties should comprise:

The analysis and sampling of all raw materials and finished products as well as such analyses as are necessary in the intermediate steps of some processes in order to insure proper control. It should furnish figures used to calculate yields and perform all the analytical work in connection with investigations, which often involves the necessity of inventing new methods. It should do all analytical work that will aid the Manufacturing, Sales, Purchasing, and Construction Departments, and coöperate with the Sales Department in investigating complaints. It should also pay strict attention to investigating and adopting better methods.

If a corporation has more than one laboratory, uniform methods of sampling and analysis should be used throughout. The selection of standard methods and the very complete written description of each should be under the immediate supervision of the Chief Analytical Chemist. Their accuracy should be proved always by analyzing mixtures of known composition. The various precautions to be observed should be specifically and prominently outlined at the end of each scheme, together with the experimental data and all equations involved proving its accuracy.

These methods should be issued to the different laboratories and all chemists of the company required to strictly adhere to them, otherwise uniform methods with all their advantages, would be impossible.

The staff of the head laboratory should be organized into an analytical council holding weekly meetings, discussing at alternate meetings the company's standard methods of analysis and abstracts of promising

analytical methods from the current chemical literature. These abstracts should be incorporated in the minutes of the meetings, copies of which go to each of the laboratories of the company. This system would automatically inform the company's chemists of the atest developments in analytical chemistry. All the important chemical journals should be promptly and systematically abstracted. These condensed abstracts should be typewritten on cards and filed under subject indices. They would prove of great value in investigating methods of analysis. All investigations work along analytical lines should be carefully written up, whether results are favorable or otherwise, and these reports sent to other laboratories of the company when desired. Any new methods suggested through the literature or by any of the chemists of the company should be tried and, where an improvement is found, incorporated in the standard methods.

The policy of the analytical department should be to give its members a broad acquaintance with all the work of the department by having a system of rotation, regularly changing the work of each so that, as far as possible, every man could take part in the great variety of determinations made. This would have the further advantage of protecting the company from any constant error into which one man might fall; and as an added protection, all the work should be systematically and independently checked by more exact or by different methods than those in daily use. Each man should be held strictly responsible for the work entrusted to him, his advancement depending upon himself, and he should be encouraged to become thoroughly familiar, through study and inquiry, with the theory and reasons involved.

As far as possible foremen and assistant foremen should make simple factory analyses and tests involving control of processes under them. Often a test can be made in less time than it takes to send the sample to the laboratory; of course such work should be systematically checked by the laboratory.

In order to estimate each man's capacity and to charge up the analytical work properly, the following system should be used: An analytical order should be made for each sample which comes to the laboratory and on the back of this order is recorded the amount of time spent by each chemist in making the analysis. When completed these orders should be filed under the various departments for which the work is done, and from them calculated a monthly statement of analytical charges, the material used being based upon the cost for the previous year. This system would make it a simple matter to note the progress of the analysis and the amount of work carried on by the different analysts.

The laboratories of the separate works should be strictly subordinate to the superintendents, except that all standard methods of sampling and analysis be standard methods of the company, and superintendents and chemists should coöperate for their strict enforcement.

Salaries of chemists in this department should be standardized as far as possible, and promotions made to the following positions according to kind of talent: Works Chemist, Assistant Superintendent, Research Department as Research Chemist, the Head Laboratory as Chief or First Assistant. All men engaged should be informed of this system, hired on a month's trial, and only really promising men retained.

The following methods of advancing the efficiency of the department should be employed.

(1) Systematic visits to the different laboratories of the company by the Chief Analytical Chemist in order to see that the standard methods are being properly used and to pass on the general efficiency of all the company's laboratories.

(2) Occasional visits by the Chief Analytical Chemist to laboratories of other industries, in order to incorporate in the organization favorable developments made by others.

(3) Periodical meetings of the analytical chemists to promote cordial coöperation and to discuss specific subjects.

(4) The automatic exchange of chemists between the different laboratories to broaden the experience of the company's chemists.

(5) Monthly reports should be made by each laboratory of the company to the Chief Analytical Chemist, explaining all difficulties encountered in general work and also making suggestions for improvements in existing methods. This plan would make it possible for all the company's chemists to constantly and systematically coöperate and increase efficiency.

The organization of each of the laboratories of the company should conform to that of the head laboratory.

All laboratory buildings should be roomy, light, well ventilated, and equipped with all facilities required for accurate work. The efficiency and future of men is seriously impaired by unhealthful, discouraging surroundings.

The Head Laboratory and Office should have an extensive library and subscribe to all important periodicals. All works laboratories should have at least standard works of reference.

It would be important to have the Research and Head Analytical Laboratories in the same building, with the economy of having a library in common, and coöperation in many ways. This building should be located in one of the large works of the corporation, thus making available its mechanics for the various construction and repair work always necessary, together with the advantage of advice upon many practical matters from the works superintendents; there would result also the greater facility for consultation among members of the chemical staff.

The accuracy of balances and weights, of measuring apparatus, thermometers and hydrometers, should not be taken for granted but proved to be accurate by comparison with standards of known accuracy as often as required. All standard solutions should be checked by the head of the laboratory or his first assistant. All important determinations should be made in duplicate.

All clerical work and calculations should be checked. Systems of weighing, manipulation, etc., devised to prevent errors, should be employed and rigidly adhered to, even in the simplest determinations.

CONCLUSION.

The forms of organization described above should never be allowed to fall into the rut of dull routine, but the personnel of the men engaged in this work maintained at the very highest standard, and all the necessary plans as described carried out with enthusiasm, earnestness, and thoroughness. The personal coöperation of the men of this department with members of other branches of the organization would prove an important aid in maintaining interest in the work, and be mutually educating.

These departments should lead the way so strikingly as to be apparent to all; if mediocrity were tolerated, then this branch of the organization would be indeed far from the ideal that should be its governing spirit.

LAUREL HILL, N. Y.

THE ELECTRICAL PRECIPITATION OF SUSPENDED PARTICLES BY THE COTTRELL PROCESSES.[1]

By LINN BRADLEY.

In previous articles which have been published in THIS JOURNAL, **1**, 686, **2**, 372 and **3**, 542 and elsewhere, Dr. Cottrell has explained the original work on these processes and has also described the general operation of several installations, more particularly in the metallurgical fields. The application of the same to the Portland Cement Industry forms the subject of another paper by Mr. Walter A. Schmidt (THIS JOURNAL, **4**, 719).

The problem of removing suspended particles from gases becomes a serious one when the volume of gases is very large, or the temperatures high, or when the gases contain materials which exert a corrosive action upon flues, chambers and apparatus.

The variety of problems and conditions is very large, but they may be divided into three general classes as follows:

First.—Where the composition of the gases is such that they are the cause of complaint on the ground of nuisance and damage to property.

Second.—Where the values contained in the gases render their recovery quite necessary on the ground of economy, but where the gases do not constitute a nuisance.

Third.—Where the gases may be considered sufficient cause for complaint, and yet contain values which should be recovered.

In the first class, and as a further illustration of the growing range of application of these processes, may be mentioned the black smoke, ashes and cinders coming from the stacks of some of the large power plants where the boilers are being forced. In some of these plants the operating departments have endeavored in various ways to purify their gases, so as to avoid any complaints. In a small plant, with proper arrangement of boilers, arches, settings and flues, the stack gases seldom give rise to complaint. Undoubtedly the proper method of attacking this problem is to endeavor to obtain proper combustion. However, there are a great many instances where complete combustion is not desired, and in such cases these processes may prove to be of value in overcoming the nuisance due to black smoke or other suspended particles. Among its other activities the Research Corporation is at present engaged in demonstrating the removal of such suspended particles by the electrical precipitation processes at the New York Edison Company's Waterside No. 2 Station, one of the largest power plants in the city of New York. In this plant there are nearly one hundred boilers, connected to four smoke stacks, approximately three hundred feet high by twenty-two feet in diameter. The average velocity of the gases through these stacks is estimated at thirty-eight linear feet per second. During the evening, when the peak load is on the station, it is necessary to force the boilers, so that they are delivering perhaps 100–150 per cent. in excess of their rated capacity. Automatic stokers are used, but even with the greatest care, considerable ashes and cinders are caught up by the draft and carried toward the stacks. The cross flues have been enlarged in order to reduce the velocity of the gases, but although some of the heavier particles are deposited in these chambers, the exit gases carry a fairly large amount of cinders and ashes. Experiments upon this particular material indicate that the greater portion of the large particles can be caught if the velocity in the flue is reduced sufficiently and ample time is allowed for the particles to settle out of the draft by gravity; but flues large enough to produce this result would be prohibitive. Some particles are so light that a slight movement of the gas easily keeps them in suspension. If we endeavor to increase their weight by water sprays or similar means, we interfere with the draft, and may not find our efforts successful, because some particles resist moisture and are extremely difficult to remove by this method. If we are able to construct an apparatus, which will not be prohibitive in size, and does not seriously interfere with the draft, whereby we can overcome the buoyancy of the particle in the gas and remove it from the influence of the draft, we shall succeed in cleaning the gas of the suspended particles. The actual net amount of energy necessary to withdraw these particles from the moving gas is very small indeed. The problem is to design and construct such an apparatus, then to place the electrical charge upon the particle and introduce sufficient energy to compel the particle to migrate to some point away from the rapidly moving gas. This may be accomplished by the use of high-tension direct current, either intermittent or continuous. Discharge electrodes and collecting electrodes are placed in a chamber and the gas containing the particles passed between them. The gas is ionized and some of the ions collect upon the particles, thereby charging them electrically. Inasmuch as the charged particles are within a strong electric field of constant polarity, they are driven to

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

the collecting electrodes. The construction of these electrodes may be varied considerably, to suit the special conditions of each particular problem. In most instances, the collecting electrodes are grounded. To meet different conditions, various forms of electrodes are used. The voltages used range from 15,000 up to as high as 50,000 or more, depending upon the size of installation and conditions of the gases to be treated. It will be realized that it is desirable to operate on gases at a high velocity and during a short period of time, in order that the installation may be made as small as possible. Results at present in hand indicate the feasibility of removing the cinders, ashes and black smoke from these power-house gases at a reasonably high velocity and without any serious interference with the draft.

Much more might be said about this problem, but it may be more to the point, in this general survey, to mention some phases of the work bearing upon other industries.

Shortly after the organization of the Research Corporation, last February, investigations were undertaken for the Raritan Copper Works, Perth Amboy, N. J., on the gases arising from the smelting of the slimes obtained in electrolytic copper refining. The copper, as received at the electrolytic refinery, generally contains some gold, silver and other precious metals, as well as arsenic, selenium, tellurium and many other elements, in small quantities. During the purification of the copper by electrolysis, most of these impurities settle out from the electrolyte. This sediment, called electrolytic slimes, is then treated in another department, primarily for the recovery of the gold and silver. It is common practice in some refineries to dry this slime and then give it a furnace treatment. The volatile elements are driven off in the gaseous state and subsequently condensed in the flue. During the furnace treatment, considerable silver is vaporized, some of which condenses quite near the furnace exit. At this point in the flue, dust may be found assaying very high in silver. Considerable gold may also be found at this point, probably having been carried over mechanically. Further along the flue, arsenic, antimony, selenium and other elements, or their compounds, condense, thus forming a thick chemical fume. It is interesting to note the tendencies of the various compounds to deposit. For instance, some of the silver compounds or metallic particles are very light and finely divided, and it is extremely difficult to effect a satisfactory recovery by settling chambers, centrifugal dust apparatus or by water sprays and scrubbers. Gold has been found a long distance from the furnace, but as a rule it is the first to deposit. The influence of one or several volatile metals upon the volatility of other metals, especially at various temperatures, has not been studied very extensively, but most authorities state that the loss of silver is increased in the presence of lead or zinc. Probably arsenic or antimony also exert an influence upon silver. It would be interesting and of considerable value to be able to consult curves of vapor tensions of these various elements under the varying conditions of these refinery gases. Samples of this kind of dust from various refineries show it to have a range of at least from 100 2000 oz. of silver per ton. The gold content is not apt to vary so greatly. Fume has been collected after passing through water scrubbers (so arranged that the gas was saturated and carried water particles in suspension) and found to still contain large amounts of precious metals. The character of the fume will depend, of course, upon the composition of the copper received at the refinery, as well as upon the operations of the refining furnaces. It is almost impossible to filter this gas, because of its corrosive action upon the filtering medium, and its tendency to clog the same. Results obtained upon these gases lead to the conclusion that practically all of the values can be readily recovered by the electrical precipitation processes, thereby insuring a greater net profit in these departments. The problem of recovering the values from the dust collected is receiving considerable attention. If all the collected dust is fed back into the furnace, the highly volatile elements will again be driven off, subsequently condensed and, in turn, collected. This will permit the impurities to concentrate and increase to such a point as to be objectionable. Experiments are now being conducted with a view to facilitating the recovery of the precious metals in a pure state from this precipitated fume. The proposed method may open up an opportunity for improvements in the present practice of treating these electrolytic slimes.

Arrangements have also been made to install the processes upon the gases from the copper converters at the Garfield (Utah) Smelter of the American Smelting and Refining Co. The fume contains considerable lead, and small amounts of silver and other elements. Apparatus has been installed to treat the gases from one converter, and this will be placed in operation in the very near future.

The electrical precipitation processes have been in steady use for the collection of sulphuric acid mist from parting kettles in one silver refinery for a number of years, and have given excellent results. Another application recently developed is the equipment of acid concentration stills, so as to recover the small amount of sulphuric acid being carried away by the gas. The installation is very compact, the power consumption small, and very little attention is required. For installations of this character special devices for overcoming insulation difficulties and promoting the ionization by the discharge have had to be worked out. The pubescent electrodes are one of the most important features in installations of this type.

The Ohio and Colorado Smelting and Refining Company at Salida, Colorado, one of the large lead smelters in the western portion of the United States, is installing the processes on their roaster stack. Godfrey machines and Dwight-Lloyd sintering machines are employed, delivering their gases to a common flue. This flue has a cross section of such size that the average velocity of the gases is about 500 linear feet per minute. A large amount of the very

heavy particles are deposited in the first 200 feet of flue, but the fume is being discharged from the stack, after having traveled a much greater distance. Preliminary tests were made on these gases at a point about 150 feet from the stack base. The temperatures varied from 100° C. to 150° C. During these preliminary tests, the ore charges upon the sintering machines were varied and checked against the assays of the dust recovered electrically, during the day, in order to ascertain how the different charges influenced the loss of lead. Assays of recovered dust varied from 20 per cent. to 45 per cent. lead during this period. Even at this distance from the roasters, considerable silver and an appreciable amount of gold were found in each sample. The dust recovered was dry and could easily be handled, as it was so dense and compact that a little draft did not blow it away. The smelter is now proceeding with an installation on a larger scale and it is expected that considerable values will be recovered. Furthermore, this installation may make it possible to push the roaster department to a greater tonnage, due to the ability to collect any materials carried in suspension by the gases. In some roasters, a fairly large percentage of sulphur trioxide is produced. Apparatus can easily be designed to handle this character of gas successfully, without undue deterioration.

Another recent application of these processes is in the removal of tar and suspended carbon from illuminating gas. Mr. Walter A. Schmidt has directed the work upon the gas manufactured from crude petroleum at one of the gas plants near San Francisco. A complete clearance of all visible particles was obtained. In the eastern part of the United States, the work of Prof. A. H. White, of the University of Michigan, should be mentioned. Under the auspices of the Michigan Gas Association, Prof. White has conducted extensive investigations, primarily upon the removal of tar from gas manufactured from soft coal. The results were so gratifying that negotiations have been instituted for a larger installation, for this purpose. The tar is collected upon the collecting electrodes and runs off into sealed chambers. This field promises to be a very wide one.

Several months ago, prior to the organization of the Research Corporation, Dr. F. G. Cottrell made arrangements with Prof. R. K. Duncan, of the University of Pittsburgh, whereby the latter arranged to use the Cottrell processes for conducting investigations upon the smoke problem of the city of Pittsburgh. Dr. Strong, Dr. Benner and others have been of assistance in this important problem.

Many other problems of a nature similar to some of those mentioned above have been brought before us and an effort will be made to adapt the processes to them at the earliest possible date. There are many places adjacent to New York City wherein considerable values may be recovered and at the same time, improve the atmosphere, at least in so far as suspended particles and obnoxious fumes are concerned.

Much more of the details of the processes themselves or their application to specific problems might be given, but it would prolong this paper unnecessarily I sincerely trust that the above general survey may be of value as well as interest to the chemists and engineers.

NOTE. Mr. Bradley explained in detail the construction of the small apparatus prepared for demonstrating the Cottrell processes. The first test was upon the precipitation of cement dust, which was blown through a pipe 6 inches in diameter. The effect of the high tension current was to collect all of the dust within the pipe. A test was next made upon some chemical fumes. Compressed air was blown through bottles containing concentrated ammonia and concentrated hydrochloric acid, separately, and the chemically laden gases mixed in a chamber just prior to being introduced into the electric treater. Dense fumes of ammonium chloride were thus obtained and the effect of turning the current on and off was demonstrated. Samples of the various materials, which were collected by the processes in large scale operations, were upon the desk for inspection.

THE CONTROL OF TEMPERATURE IN THE OPERATIONS OF ANALYTICAL CHEMISTRY.[1]

By THEODORE W. RICHARDS.

The control of temperature is a very important question in the work of the analytical chemist. The reason is at least three-fold. In the first place, temperature affects greatly the speed of all chemical reactions which are generally accelerated to extents varying perhaps seven to twelve per cent. by each degree's rise in temperature. In the second place, temperature affects the final equilibrium attained by many reacting systems and therefore influences both the yield and the composition of the products dealt with by the analyst. In the third place, accurate physical measurements, to which the quantitative experimenter must frequently resort—such as weighing the measurement of the volumes of gases and liquids, and the determinations of calorimetric or electrical magnitudes—demand considerable control of temperature if any accuracy is sought.

Clearly, the subject is too large for the brief ten minutes to be devoted to it; but a few words may be able to point out the more vital features.

Let us begin with the control of temperatures near that of the room. In the first place, it is clear that every chemical laboratory may advantageously have a thermostat attachment to its heating arrangements. For years I have used a commercial contrivance which, when operating properly, has kept my laboratory at 20° C. within half a degree, greatly to my satisfaction. In order to attain any such constancy, the air of the room must be efficiently agitated by means of an electric fan; just as any other form of thermostat should be adequately stirred. Of course, when an operation affected by currents of air is undertaken, the fan must be temporarily stopped.

Entirely within this room, surrounded by glass walls and without any outside windows, is built a

[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

balance-room, which resembles a huge balance case; and this remains constant for long periods within one- or two-tenths of a degree, because the somewhat larger fluctuations of the outer room do not quickly pass through the glass walls. The plan has worked so excellently that all balance-rooms in the new Wolcott Gibbs Memorial Laboratory at Harvard are to be built in this way entirely within other rooms.

A very suitable, sensitive, and easily constructed thermostat attachment for regulating the temperature of a room is the sealed hydrogen manometer, with electrical contact.[1] This consists of a large sealed bulb containing hydrogen, which gas is arranged to support a column of mercury having an electrical contact at its upper end—the affair is a combination of a gas thermometer and a barometer. The rapid heat conduction in hydrogen makes this gas especially suitable for the purpose. We have used the device for many years with great profit, and by its aid have been able to keep a cellar laboratory, which is protected by double windows, within 0.1 degree for weeks at a time. The electrical current, made and broken at the mercury surface in the top of the manometer by the fluctuations of the expanding or contracting hydrogen, may be made to operate a relay which in turn regulates the heating apparatus, whether this uses steam, hot air, gas or electricity. A form in which the current running through the mercury in the manometer itself is used for heating has recently been described,[2] but I should be afraid that this might not be able to maintain quite as accurate a constancy as an apparatus using a weaker current in its regulating manometer.

Often the yet more accurate regulation of the temperature of small objects is needed; of course the Ostwald toluene regulator in a bath of water or oil gives the most convenient thermostat for such purposes. Of late we have used, on account of its cleanliness and safety, only electricity as a means of supplying heat to this bath; the regulator is arranged so as to make and break a feeble electrical circuit which operates a relay through which in turn runs the stronger heating current. The chief, probably the only disadvantage of electrical heating, is the possible leakage of electricity. If it is used for electrochemical work, one must guard against stray electromotive forces by efficiently grounding the thermostat. The description of an arrangement of this kind making possible the maintenance of the temperature within 0.001° or 0.002° for days is perhaps not out of place. This has been used at Harvard for many years; it was briefly described several years ago and has been used independently by others.[3]

The thermostat consists of a large can which may be as large as 70 centimeters in diameter and 70 or more high. The can is covered on the outside with felt and may have its surface protected with oil if evaporation is to be prevented. Within this can is immersed a regulator similar in principle to the toluene thermostat regulator of Ostwald. The receptacle for the toluene is made with five large fingers having walls of moderately thin glass, and is arranged to have a capacity of over half a liter. The mercury column, raised and lowered by the expansion or contraction of this toluene, "makes" and "breaks" a feeble electrical circuit which governs through a relay the stronger current used for heating. The latter current passes through the relay and through a large insulated heating coil immersed deeply in the water of the thermostat.

The "making" and "breaking" happen advantageously in a somewhat narrow tube, perhaps two millimeters in diameter, and the mercury in this tube should be protected from the laboratory air by an atmosphere of pure hydrogen, supplied by a very small automatic hydrogen generator attached to the apparatus. This device is very important if great constancy is sought; it constitutes the only unusual feature of our apparatus.

The efficiency of this regulator, or indeed of any other, as a means of keeping the temperature constant depends greatly upon the agitation of the water in the thermostat. This should be violently stirred by means of a rather powerful motor in order to keep the temperature constant throughout and to effect a rapid exchange of heat between the bath and the toluene regulator. The degree of agitation usually employed is entirely inadequate. The temperature is obviously much more constant if the room containing the thermostat is allowed to vary but little in temperature; it is advantageously kept perhaps a degree below the temperature of the bath. By running a thin pipe containing cool water around the inner circumference of the top of the bath, compensation for a higher temperature may be easily obtained. If care is taken and the glass toluene receptacle is sufficiently large, and is well seasoned so that it has assumed a reasonably constant volume, the thermostat will keep constant within one- or two-thousandths of a degree for weeks.

This arrangement makes no pretense to novelty in principle, but in efficiency it probably exceeds most other forms because of the details needed in its construction. A very similar apparatus has been more recently described by Hulett,[1] but he does not seem to have sought or attained quite the degree of precision which we have successfully employed.

Very satisfactory thermostats may be made from baths filled with pure salts in the act of transition from a state of greater to a state of less hydration. Such mixtures keep a striking degree of constancy for a long time. Sodium sulphate is the best substance for this purpose. For details a paper by K. L. Mark and the present author in Vol. 38 of the Proceedings of the American Academy of Arts and Sciences should be consulted.

The control of low temperatures and of high temperatures has received so much general notice recently that this expert audience needs no detailed exposition of these topics. The employment of pure ice for maintaining a definite degree of coolness is known to every one, but the almost equally serviceable

[1] Regand and Fouillard, *Z. wiss. Mikroskop.*, **20**, 138 (1903); also Richards and Mark, *Proc. Am. Acad.*, **41**, 119 (1905).

[2] Bonsfield, *Chem. News*, **105**, 13 (1912).

[3] Richards, Carnegie Inst. Washington, *Pub.* **56**, 22 (1906); **76**, 9 (1907).

[1] *Physical Review*, **32**, 277 (1911).

use of ice mixed with solutions of definite concentrations for increasing coolness is perhaps less generally recognized.[1]

For example, ice mixed with dilute hydrochloric acid containing 28.19 grams of hydrogen chloride per liter gives a perfectly constant temperature of —3.00°.[2] Of course, if heat is added, some of the ice melts, the solution becomes more dilute, and the temperature rises. This, however, may be easily prevented by enclosing the constant-temperature bath by another bath containing a mixture having the same freezing point. If an air space (or still better, the evacuated space of a Dewar vessel) is placed between the two baths, the inner one will maintain an amazing degree of constancy for long periods of time, particularly if more dissolved substance from time to time is added to the outer vessel as its ice melts. The lower limits of the temperature attained in this way are of course the cryohydric temperatures of the more soluble substances.

Lower temperatures are customarily obtained by means of solid carbon dioxide with alcohol or ether, and still lower ones by liquid air and hydrogen. By boiling the liquefied gases under reduced pressure their temperature-range may be extended considerably. The details of working with these now familiar substances need hardly find a place in this brief review. Acquaintance with the necessary technique is becoming more and more an essential part of the complete chemist's outfit, although analytical operations rarely demand low temperatures.

Turning now to higher temperatures more frequently employed by analytical chemists, wide limits must receive consideration. Open steam baths are essential, and are too well known to need discussion. Thermostats of concentrated salt solutions or oil or paraffin, or of fused mixed sodium and potassium nitrate, may be used at fairly high temperatures, if proper regulating devices are employed. For most purposes, however, air baths regulated either by thermostat control or by approximately constant steam, gas, or electrical heating are more commonly employed. If steam under constant pressure is available, it forms a very usual and convenient means of maintaining constant temperatures somewhat above 100° of the needed in analytical laboratories. Gas, or more recently, electrical heating is more commonly used; the latter has the great advantage of cleanliness. Other vapors also, such as toluene (110°), the xylenes (140°±), and aniline (184°) are often used with advantage. Air baths without thermostat attachments are usually arranged to maintain only a certain difference between the room temperature and the higher temperature sought. This is all very well if the room remains constant in temperature, but sometimes laboratories change as much as 10° or 15° during the day, and this change may have serious effects in some delicate operations when it reappears in the heated air bath. For such operations a thermostat regulation of the temperature of the bath is almost essential.

The forms of air bath which have been proposed are countless. Most of them lack the needful requisites of resistance to corrosion and therefore of cleanliness. The utensils containing the substance to be heated usually needs to be protected by some form of shelter or roof, such as a watch glass, to keep out particles of impurity from the corroded walls of the oven. This is altogether unfortunate; the air-bath used by analysts should be free from such defects, therefore it should be made of glass or porcelain.[1] It is almost needless to point out that for many purposes the products of combustion also should be rigidly excluded from the inside of the oven if gas is to be used as a source of heat. Moreover, the air of the laboratory is often injurious to sensitive substances; such material should be heated in boats within tubes, even if only dried at 100°. The well known "bottling apparatus," so much used at Harvard, makes this precaution easy.[2]

For higher temperatures burners of various shapes are available, and more and more use is being made of the yet greater possibilities of electrical heating.

Most of the gas burners are either modifications of the Bunsen burner or the blast lamp, and some of the former, especially the Meker burner, have been made of such efficiency as to replace for many purposes the use of air under pressure. To obtain a constant temperature with these burners, it is necessary usually to attach to the gas supply a contrivance for giving it constant pressure; otherwise the fluctuations are considerable. It is needless to point out that contrivances for preventing radiation, such as clay cylinders and other forms of furnaces, greatly promote the constancy of temperature attained.

Turning now to electric heating, we have not only the electric furnace so much used in technical work, but also, more suitable for analysts, a sort of electric muffle, a porcelain or other refractory tube wound with resistance wire, capable of producing and withstanding the high temperatures needed. For temperatures up to 1000° the alloy called "nichrome" works very well as the material of the resistance wire; for higher temperatures platinum is necessary, but even that is less refractory than one might wish. We have obtained excellent results with the type of furnace made in this fashion with tubes of pure silica as core. The maintenance of constant voltage and even conditions of radiation provides the operator with a very fairly constant temperature, which is most conveniently estimated by the platinum-rhodium thermopile.

In summing up, it may be said that attention has been called to the relative advantages and fields of usefulness of some of the more important methods of controlling temperatures between 3000° and —250°. A few of the most essential details of execution have been suggested and emphasis has been placed upon the frequent importance of constancy of temperature and of the exclusion of outside impurity.

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[1] This was suggested by Roloff, *Z. phys. Chem.*, **18**, 572 (1895).

[2] Richards and Jackson, *Proc. Am. Acad.*, **41**, 473 (1906).

[1] A simple, clean, and inexpensive electric oven is described in *Am. Chem. Jour.*, **22**, 45 (1899).

[2] See, for example, the Faraday lecture of 1911, *Jour. Chem. Soc. Trans.*, **99**, 1203 (London).

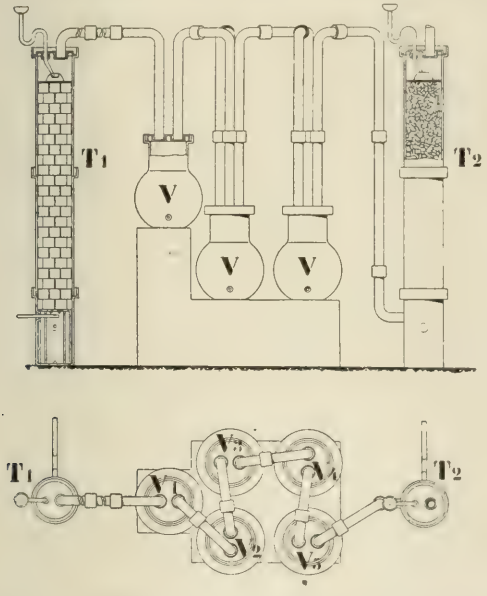
CURRENT INDUSTRIAL NEWS

By W. A. Hamor.

"VITREOSIL" IN THE NITRIC ACID INDUSTRY.

"Vitreosil" has not been so extensively used in the manufacture of nitric acid as in the sulphuric acid industry. This is attributable to the difficulties encountered in manipulating molten quartz and to the fact that retorts, receivers, etc., used in the manufacture of nitric acid are larger than could be made until recently. However, smaller forms of apparatus intended for such a purpose, as conduits and still-heads for the Valentiner apparatus, still-heads for the Guttmann system, and built-up pipe ranges and condensers, have been on the market for some time, and recently "vitreosil" denitrating towers have been announced.

"Vitreosil" denitrating towers are an improvement over those of earthenware, as they allow the use of superheated



steam; as is well-known, stoneware has the disadvantage of liability to break through temperature changes. The whole apparatus illustrated herewith is constructed of "vitreosil." The usual size of the tower T_1 is 250 mm. in diameter and 2290 mm. in height, and it consists of three tubes, each about 760 mm. in length. When a tower of this size is heated with steam at 200° C., and the nitric acid present amounts to 5 per cent., 8 tons of mixed acids may be denitrated per 24 hours. The superheated steam enters through a tube in the center of the base, and the tube is so formed that the steam can only move upwards. The nitric acid vapors are conducted from the upper part of the tower T_1 to an air-condenser which is composed of five "vitreosil" condensation vessels (V) of 75 liters content. The exit gases are led into an end-tower (scrubber) T_2 which is packed with pieces of quartz. The whole apparatus is compact.

DEVELOPMENT OF THE SULPHITE INDUSTRY.

In a recent lecture before the Austro-Hungarian Cellulose and Paper-Stuff Association, an interesting résumé of the beginnings and progress of the sulphite pulp industry was given by E. Spiro, from which the following is extracted by *Paper*, 9, No. 7, 25.

B. Tilghmann, of America, took out an English patent in 1866 for a process of obtaining cellulose from wood. The essential feature of his method was boiling the wood with solutions of bisulphites of the alkalies or alkaline earths. Tilghmann's patent was a failure, and it was not till more than ten years later that Mitscherlich, Kellner, and Ekman put the manufacture of sulphite pulp on a commercial basis.

The manufacture of sulphite pulps consists of four stages:

1. The mechanical preparation of the wood.
2. The preparation of the lyes.
3. The boiling.
4. The breaking up of the boiled wood, and the rinsing, sorting and drying of the separated fibers.

In the time of Mitscherlich the knots were drilled out and the wood then cut up with circular saws into lengths of about an inch and a quarter. This procedure had several disadvantages. It was expensive and tedious, and, like every other process involving the use of the circular saw, very dangerous to the work people. Accidents were constantly occurring. Again, the thick discs of wood required long boiling in very strong lye. Against all this, however, we have the fact that the cellulose obtained was stronger than has since been got by more modern processes. The sawdust was boiled up with the discs for economy's sake, and inevitably contained portions of the knots. These impurities caused numerous dark specks in the finished pulp. Dark specks also often appeared in the pulp for another reason: the high temperature prevailing during the boiling under a pressure of several atmospheres, reached the interior of the discs before the lye and actually charred the still dry wood.

Cutting the discs thinner was, of course, a remedy, but involved the expenditure of more money and time in the sawmill.

Ritter, Kellner, Ekman, Flodquist, and Francke used revolving chopping machines, and so reduced the waste that it could be neglected and did not have to be boiled up with the lye. When the sawmill was used, so much sawdust was produced that it was imperative to work it into cellulose as well as the discs.

Kellner was the first to see that the wood had to be divided into smaller pieces. Hence he originated the application of a grinding process to the chips. His grinding apparatus consisted of a series of conical cast-iron grinders revolving on a vertical axle. These grinders were ribbed, as was the interior of the chamber in which they revolved. The chamber was, of course, provided with a hopper above for feeding in the chips and with an outlet below for the ground stuff. The wood was divided in this mill parallel to the direction of the fiber, and the previous removal of the knots was supposed to be avoided. As a matter of fact, the reverse was the case. The grinding simply broke up the knots so small that the impurities were widely distributed through the pulp. He was, therefore, obliged to return to the method of removing the knots before grinding. This he did with special machines, comprising very small circular saws revolving at a very high speed. At the same time, he found that a specially constructed chopping machine was necessary to get pieces small enough to be properly ground in the mill.

The use of this machinery was found to entail considerable danger to the workmen, with its attendant consequences of actions for damages and demands for higher wages. Hence the introduction of the centrifugal mill with an axle armed by steel spikes revolving in a chamber from the inner walls of which similar spikes project. Even with the mills it was impossible to prevent the occurrence of knot débris in the pulp, and this had to be sorted out by perforated drums, similar to those used for sorting broken stone. These imperfections have led to the

introduction of the present roller-disintegrators. Another application of the centrifugal principle is in sorting the chips. If the chopped wood is centrifuged in a suitable machine, the heaviest and largest pieces are separated from the lightest and smallest fragments.

Mitscherlich's tower plant, although it has been altered in details, is still largely used. His original towers were built up of casks with the heads and bottoms knocked out. They are now usually made of granite.

The sulphurous acid is made by roasting iron pyrites in ovens such as are used in the manufacture of sulphuric acid. The hot gases pass from the ovens through brick channels into cast-iron pipes, which lead them into a set of vertical pipes, having about two-thirds of the height of the tower. From this set they travel downwards through another set of vertical pipes of the same height so that they enter the tower at the bottom. The object of passing the gases through the two sets of vertical pipes is to cool them, and also to increase the current passing into the tower. The descent of the cooler gases in the second set of vertical pipes exerts a kind of suction which draws the hotter gases up the pipes of the first set. At the same time, the current of gas varies with the weather, being quicker in cold weather than in hot, and slower with a high than with a low barometer. The tower itself is, of course, filled with limestone to absorb the sulphur dioxide and form the bisulphite for the treatment of the wood. This is delivered in the form of solution ready for use at the bottom of the tower, water being continually sprinkled over the carbonate of lime from the top of the tower.

Kellner's attempts at improving this plant were not very successful. They were directed chiefly to making the working of the tower uniform, or, in other words, independent of those atmospheric influences just mentioned. The only practical result took the shape of introducing intermittent artificial draught, used, of course, when the atmospheric conditions were adverse to the free passage of the gases. Another idea of his was to substitute, for the single lofty Mitscherlich tower, several lower ones. In this type of plant the water is supplied to the last tower only, and the weak lye from the bottom of it is pumped to the top of the last tower but one. It arrives at the bottom rather stronger, and is straightway pumped to the top of the last tower but two, and so on. This necessarily demands several acid-resisting pumps and much power.

PROBLEMS IN PAPERMAKING.

Schwalbe calls attention (*Paper*, **9**, No. 5, 23) to the chemical problems which abound in the paper mill. There is the question of the influence of chemicals on the "beating" process. Cellulose is a colloid, and, as such, should be responsive in a physical sense to the action of very small quantities of chemicals in solution. The bleaching problem has been very little studied on the chemical side; it is not known what is the exact nature of the substances removed from the pulp by bleaching nor in what form they are eliminated.

The problem of sizing remains full of unsolved points and chemists are not agreed even on the simplest question of the chemical reactions, while the physical reactions are still more obscure. The fixation of the loading materials is a physico-chemical problem which should repay systematic investigation. All mineral loadings, especially clay, are colloidal and readily influenced by traces of soluble salts.

The question of new sizing agents is waiting solution and the utilization of waste resins from the rubber industry appears to be within sight. Under certain conditions engine-sized paper loses its resistance to ink after storage, and the chemical causes of this loss are still unknown.

In dyeing the pulp, the chemical relations of the dyestuff have to be studied, not merely towards the fiber, but also towards the mineral loading materials. Finally, there is the problem of the clarification of the machine waste waters and the recovery of useful material from them; there is every probability that the mechanical process of clarification might be materially assisted by suitable chemical additions.

THE AUTUMN MEETING OF THE INSTITUTE OF METALS.

The autumn meeting of the British Institute of Metals took place at the Institution of Electrical Engineers, in London, on September 25 and 26, 1912, and a number of interesting papers were presented. The report which follows was taken from *Nature*, **90**, No. 2242, 199–201.

Two papers dealt with the joining of non-ferrous metals and alloys. In these Carnevali and Tucker discussed the question of autogenous welding. Owing to the great extension of autogenous welding by means of oxygen and acetylene, the question as to how far the results of this process can be depended upon is an important one. Tucker appeared to regard a weld as satisfactory if it is found on testing it to destruction that the fracture occurs away from the weld itself; but Carnevali pointed out that the weakest portion of a welded joint is not the weld itself, but the region of injured metal on either side of it. According to Carnevali, the strength of welds in copper and its principal alloys can not be depended upon, and this conclusion agrees with the views on autogenous welds in iron and steel recently expressed by Fremont and others. With regard to pure aluminum, however, Carnevali found the method to give satisfactory results, but the efficiency of a weld was much reduced as soon as it was applied to one of the stronger light alloys of aluminum. To quote *Nature:* "Broadly speaking, these papers lead one to view the rapid development of autogenous welding practice with some suspicion."

A paper by Law dealt with oxygen and oxides as deleterious impurities in alloys. He took the view that progress in non-ferrous alloys was largely a question of the better elimination of oxides, and this opinion was supported in the discussion by Rosenhain. Turner appealed to chemists to devise a satisfactory method for the determination of oxygen in brass. Johnson dealt with the effect of impurities, chiefly antimony, on the properties of tough-pitch copper, and here again the discussion centered around the part played by oxygen. The lenient view as to the deleterious effects of antimony put forward by Johnson was vigorously opposed by those who have to deal with copper on the large scale.

Carpenter contributed two papers dealing in minute detail with the inversion which he has discovered in a certain range of copper-zinc (brass) alloys at a temperature of 470° C. In one of these papers he dealt with the effect of impurities on this inversion and found that any addition of a third metal to these alloys tends to facilitate rather than to inhibit the transformation in question; since the change renders the metal weak and more brittle, it is evident that the use of the purest copper and zinc is desirable in the manufacture of those varieties of brass containing the constituent.

Rosenhain and Ewen presented a paper on the intercrystalline cohesion of metals. They advanced the view that the crystals of a pure metal are held together by the action of a thin layer of metal in the amorphous condition forming a kind of cement between the crystals. The conception of the existence of such a cement, we may note, had already been put forward by Bengough and by Osmond, but Rosenhain and Ewen claimed to have used it as a working hypothesis in their own laboratory before others had published their views.

Beilby discussed the phenomena of the solidification of metals from the liquid state in reference to the "foam-cell" theory of Quincke. The fundamental question, which goes beyond Quincke's hypothesis, is, whether the metal in a liquid state undergoes any changes or separations before actual solidification commences, and, if so, whether there is really any formation of

foam cells or analogous structures governing the crystallization of the metal. Beilby evidently finds the "foam cell" theory less attractive after close consideration. It is likely that an exhaustive report on our present knowledge of the passage from the liquid to one solid state in metals, will be prepared under the auspices of a committee of the Institute of Metals; this will certainly be very welcome to metallurgists and chemists.

SOLID OIL AS A MARINE FUEL.

The question of a solid fuel for ocean liners in the shape of solidified petroleum is being taken up in Europe, and the outlook for this kind of fuel seems promising according to the *Scientific American*, **107**, 326. Tests have been made in many countries with spray fuel burners, but when it came to actually applying these on shipboard an obstacle arose, as the new method would lead to a radical transformation of the existing apparatus. Besides, great storage tanks are needed for the liquid, and the action of the latter upon the walls of the tanks would be strongly felt when the vessel is rolling at sea. It was decided quite recently at a meeting of ship owners at London to go into the production of solidified petroleum brickets on a large scale. These are obtained as follows: The crude oil is boiled and to it is added a certain amount of stearic acid with an alcoholic solution of caustic soda. Upon cooling, there is obtained a transparent mass somewhat resembling glycerine soap, and it has sufficient cohesion to allow of making it into square-shaped brickets. Such blocks have a slow and very regular combustion owing to their uniformity of structure. The weather does not seem to affect them, and they always remain clear. The heat production from them is such that a ton of solidified petroleum serves instead of $2^1/_2$ tons of coal. The great saving of space on shipboard is evident, and another point is the great all-round economy realized for producing an equal amount of steam. Some British naval engineers studied the question and concluded that for a single trip of a Cunard liner from England to New York and return the lowest figure for the saving would be $60,000. They also reported the following points in favor of the new fuel: 1. No appreciable modification of the furnaces or bunkers is needed. 2. The brickets burn very well in open furnaces. 3. They have a very high calorific power. 4. No inflammable gas is given off under the action of heat in the furnace. 5. They burn slowly without running of liquid, nor is there any crackling or explosion. No ash is left. 6. Their regular shape facilitates storing, and there is no space lost. 7. The brickets harden with time and reach a great crushing resistance. 8. The range of the vessel will be much increased, which is a capital point for war vessels. From another point of view, it is held that the navigation companies will be more inclined to increase the speed of the ocean liners, since they are able to obtain high steam pressure at a much less cost for fuel than before.

HIGH-PRESSURE GAS LIGHTING.

At a meeting of the New York Section of the Illuminating Engineering Society, held on October 10, 1912, G. S. Barrows presented for the authors, F. W. Goodenough, Oscar Klatte and R. N. Zeek, papers relating to high-pressure gas lighting.

High-pressure gas lighting has been employed in Germany for the past ten years and has reached a high stage of development. The lamps employed have from one to five mantles and vary in candle-power from 500 to 4000. An indication of the growth of this kind of lighting is found in the city of Berlin, where, up to 1905, about 15 miles of street were lighted with electric arc lamps. From 1905 to 1911 a mile of electric lighting was added. In 1905 about 4 miles were lighted with high-pressure gas, but, during the period from 1905 to 1911, 32 miles of high-pressure gas lighting were added, and a further extension of 42 miles is contemplated. There are several high-pressure gas-lighting installations in America, but thus far they have not passed beyond the experimental stage.

Norman Macbeth claimed that the rapid development of gas lighting in Europe as compared with America represents an indictment either of electric men abroad or of the gas men here. He claimed that the gas manufacturers in this country do not appreciate the opportunities that exist in their own field.

H. T. Owens called attention to the increasing interest aroused in high-pressure lighting, which doubles the efficiency as compared with the methods in common use to-day.

In closing the discussion, Mr. Barrows remarked that while the life of the incandescent mantles as first used for high-pressure lighting in this country was about ten days, improvements in mantles have caused an increase in life to about fifty days.

THE PROPERTIES OF MOTOR FUELS.

Romberg (*Ding. poly. J.*, **327**, 616) gives the properties of the motor oils on the German market as follows:

Title.	Density.	Setting point. B. p., C.	Setting point. C.	Use.
Galician gas oil	0.868	300°–380°	+ 1	Diesel motors
American gas oil	0.858	300°–380°	—10	"
Motor benzine	0.705/15	60°–120°	—20	Automobile and small motors
"Veloxin"	0.69/70	50°–110°	—20	"
Motor benzine II	0.75/76	90°–160°	—20	"
Automobile benzine	0.69/70	60°–100°	.	"
Motor benzine I	0.715/25	70°–120°	.	"
Motor benzine II	0.75/77	100°–140°	..	"
Automobile benzine	0.692/98	40°–110°	—70	"
Motor benzine I	0.704/15	40°–120°	—70	"
Motor benzine "Heraklin"	0.734/74	75°–135°	—70	"
Motor benzine II	0.751/58	70°–150°	—40	"
Gas oil	0.864/88	174°–360°	0	Diesel motors
Gas oil I	0.863	190°–300°	..	"
Austrian gas oil	0.860	.. ....	..	"
Petroleum	0.80	100°–300°	.	Petroleum motors

THE CONSUMPTION OF OXYGEN.

Following the increase in the employment of oxygen in the welding of metals (oxy-acetylene and oxy-hydrogen welding), etc., the consumption of the commodity has grown greatly in recent years.

The *Chemiker Zeitung*, **36**, No. 117, 1128, gives the consumption of oxygen for 1911 in 1000 cubic meters as follows:

Country.	Amount used.	Number of oxygen works. Liquefaction of air.	Number of oxygen works. Electrolytic processes.
Germany	4,000	39	3
France	2,000	9	6
England	1,100	8	2
United States and Canada	1,100	9	8
Austria Hungary	600	9	1
Italy	600	4	1
Belgium and Holland	500	5	4
Russia	250	8	1
South America	230	6	1
Spain and Portugal	100	3	1
Scandinavia	100	6	
Switzerland	80	4	1
China and Japan	40	4	
Balkans	20	3	1
Total	10,720	117	30

Altogether 145 factories are engaged in the manufacture of oxygen from the air, by means of condensation and distillation, and by the electrolysis of water. There are, in addition, a number of plants employing other processes, but the oxygen is intended mainly for medicinal purposes. In France, the average

price for 1 cubic meter of the compressed gas is from 1.50 to 2.50 francs, and in Germany from 0.80 to 1.60 marks.

"PLUMBOXAN."

At the meeting of Section 8 of the Convention "Deutscher Naturforscher und Aerzte in Münster i. W.," in September, 1912, G. Kassner presented a paper on "A New Method for the Production of Oxygen by Chemical Means."

Tessie du Montay showed that alkali manganates become soft on heating and that, on treating with steam, they decompose with the separation of alkali hydroxides. On mixing sodium manganate with sodium-*m*-plumbate in molecular proportions, Kassner obtained a smaragdine green compound, or solid solution, which he calls "plumboxan." When steam is allowed to act upon this compound at an elevated temperature, oxygen is given off; upon passing air over the de-oxygenated "plumboxan," oxygen is replaced in a very short time. Again, "plumboxan" can stand higher temperatures without becoming soft and losing its porosity than alkali manganates. It is a stable compound and forms a very good means for the production of oxygen. It is necessary that all traces of carbon dioxide, as well as dust, etc., be removed from the air before it is passed over the "plumboxan." The reaction occurs according to the following equations:

$$Na_2PbO_3.Na_2MnO_4 = Na_4PbO_4 + MnO_2 + O;$$
$$Na_4PbO_4 + MnO_2 + Air(O + 4N) = Na_2PbO_3.Na_2MnO_4 + 4N.$$

ALUMINUM ALLOYS.

In the Engineering Section of the British Association meeting at Dundee, Ernest Wilson presented a report on "Exposure Tests of Light Aluminum Alloys." Investigations made during the last ten years have shown that alloys of commercial aluminum with copper only were not satisfactory. Wilson investigated alloys in the form of wire, 0.126 inch in diameter, to ascertain the effect of exposure on electrical conductivity. The addition of iron, nickel and manganese to the low-copper alloys was found to increase both the tensile strength and the resistance to deterioration. With specimens containing, respectively, 1.16 per cent. of iron, 2.25 per cent. of nickel, and 1.78 per cent. of manganese, the electrical resistance had only increased about 9 per cent. in eleven years. "Duralumin" was a copper-manganese-aluminum alloy, plus about 0.5 per cent. of magnesium, and after an exposure of one year a specimen 80 feet long had increased 5.15 per cent. in electrical resistance. Wilson asked, was this due to the comparatively high percentage of copper or was the manganese too low? This alloy could, by suitable treatment, be obtained with a very high breaking load, but its specific resistance was about twice that of commercial aluminum.

In the discussion, Lupton pointed out the well known destructive action of salt on aluminum and its alloys. Petavel called attention to the fact that "duralumin" at its best might have the lightness of aluminum with the strength of steel, but, unfortunately, it was extremely sensitive to heat treatment.

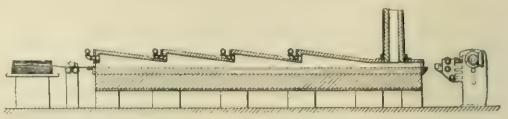
In this connection, see W. Roberts-Austen, *Third Report of the Alloys Research Committee*, wherein the melting points of the iron-aluminum alloys are given; and E. F. Law, Faraday Society, June, 1910.

METALLURGIE.

Beginning with the October number, the German journal *Metallurgie* was divided into two independent publications. One, *Metall. und Erz*, is to deal with the mining, concentration and metallurgy of ores, with the exception of those of iron, and will be edited by the Gesellschaft Deutscher Metallhütten- und Bergleute; the other, *Ferrum*, will deal with the metallurgy of iron and steel, mechanical testing, metallography, etc. *Ferrum* is edited by Dr. Wüst, of Aachen. *Metallurgie* attained a high position in technical literature, and it is to be expected that the two new journals will cover their respective fields comprehensively and will prove of more direct service to their readers who are specialists in the metallurgy of the ferriferous and non ferriferous ores.

A NEW TYPE OF CONTINUOUS FURNACE.

The oil-fired furnace illustrated herewith is the invention of P. J. Gordon and R. T. Prall; it is being used at the Youngstown, Ohio, plant of the Republic Iron and Steel Co., for heating rods in the manufacture of railroad spikes, but the idea may be capable of extension to glass and sintering furnaces.



In principle, the construction consists in having a number of reverberatory hearths in tandem. The furnace at Youngstown is $9^1/_2$ inches wide, 12 inches high at the burners, and 5 inches high at the "verbs." Either gas or liquid fuel may be used, and, when fired, the furnace has the appearance of an incandescent tube.

ARTIFICIAL SILKS.

Artificial silk is fast coming to be a very important textile material and is being used in ever-increasing quantities by the trade. It is employed as an adjunct not only to the silk industry itself but is also being used in connection with wool and cotton in the preparation of a great variety of fabrics. It is even being used largely in knot goods and hosiery in combination with cotton and mercerized cotton.

The dyer, therefore, is meeting more and more with this product, and as there are three different kinds of artificial silks in general use and as these different varieties possess certain differences in structure and quality, it really becomes a question of considerable importance to the dyer to know one variety from another. This is more especially important because one silk may stand a treatment which would be fatal to another.

The three artificial silks now to be met with on the market are described in a recent issue of the *Wool and Cotton Reporter* as follows:

1. Collodion silk, known also as Chardonnet, or nitrosilk. It is prepared from nitrated cotton.

2. Cuprate silk, known also as Glanzstoff, Pauly, Elberfeld silk. It is prepared from a solution of cellulose in cuprammonium solution.

3. Viscose silk. This is prepared from a solution of cellulose in a mixture of caustic soda and carbon disulphide.

In their outward appearance the three forms of artificial silk are so nearly alike that it would not be possible to distinguish between them. Even a microscopic examination by an experienced observer does not lead to any positive conclusion as to kind of silk.

A fairly simple test, however, and one which may be easily carried out by the average dyer is the following: A sample of the silk to be tested is placed in a small porcelain dish, and concentrated sulphuric acid is poured over the fibers. If the sample consists of collodion silk no coloration appears until about an hour has elapsed, when the acid solution will acquire a pale yellow color.

In the case of cuprate silk the acid becomes yellow immediately and the color becomes deeper on standing. In the case of viscose silk the acid immediately develops a reddish brown color, deepening to a rusty brown after standing for an hour.

NOTES AND CORRESPONDENCE

OBITUARY—THOMAS PRICE.

Professor Thomas Price, a member of the American Chemical Society, died in San Francisco, on October 13th, at the age of 77 years.

Professor Price came to San Francisco in 1862 from Swansea, Wales, of which principality he was a native. He had been professor of chemistry in the Normal College of Swansea, succeeding Greville Williams, whose assistant, pupil and friend he had been, and it is interesting, at this time, to recall that he worked with Williams on his classic separation of isoprene. Professor Price also studied at the Royal School of Mines in London where Hofmann was then professor of chemistry, and Percy the professor of metallurgy.

In San Francisco, Professor Price was for some years professor of chemistry and toxicology in the Toland Medical College, where he also took the degree of M.D. With Dr. Lane and Dr. Gibbons, Sr., he started what is now the Cooper Medical College, the medical department of Leland Stanford, Jr., University.

The mineral *priceite* was so named by Professor Silliman, of Yale, in honor of Professor Price, whose work, subsequently confirmed by Silliman and Dana, had shown it to be a hitherto unknown borate of lime.

Professor Price was always most active in his profession, almost to the end of his long useful career, and no name was better known to the profession and the laity than his. Few men anywhere have been so generally called upon as an expert witness in important cases involving toxicological or general chemical questions as was Prof. Price.

He was of a most genial and lovable disposition, a ripe scholar and a deep student, and profoundly modest withal.

Professor Price is survived by a son and three daughters.

ARTHUR F. PRICE.

A SUGGESTION REGARDING THE GRADUATION OF HYDROMETERS.

Editor of the Journal of Industrial and Engineering Chemistry:

The hydrometers, which are at present in general use, are the Baumé, the Twaddle, and the normal hydrometer. The Baumé is used especially among practical men, but it has no scientific standard and shows many inconveniences. It has two kinds of units of graduation for the heavier and the lighter liquids, and each 1 degree has a different magnitude of specific gravity; for example:

	Degree.	Sp. gr.	Difference.
Heavier liquid.....	1–2	1.0000–1.0066	0.0066
Heavier liquid.....	50–51	1.4902–1.4951	0.0049
Lighter liquid.....	10–11	1.0000–0.9932	0.0068
Lighter liquid.....	50–51	0.7849–0.7808	0.0042

The Twaddle is from the scientific view point much better than the Baumé, but it lacks that for the lighter liquid. The normal hydrometer is scientifically the most rational, but its use is limited to scientific workers. In my opinion it has also some faults, which make it unsuitable for practical men.

(1) It gives only absolute numbers, which are rarely used among practical men. When it is said that sulphuric acid has a sp. gr. of 1.710, the number is absolute; it is much clearer to say 60 degrees.

(2) The numbers have many decimal figures, which are very inconvenient to read and to remember. When it is said that the specific gravity is 1.710 or 0.807, we have three decimal figures. It is much easier to say 60 or 45 degrees.

Hence, as I think, the normal hydrometer did not come into general use among the practical men, and other various hydrometers are used which make things very complex.

Therefore, I wish to propose a hydrometer for industrial and commercial use, which will be graduated to have 1/100 part of the weight of water at 4° C. as a unit, *i. e.*, water as 100°. With this hydrometer the following conveniences would result:

(1) Its degrees would have a simple relation to the real specific gravity, and would be scientifically much more correct than the Baumé and Twaddle systems.

(2) The unit of graduation will have a name (degree), which is among practical men more convenient than an absolute number.

(3) The number indicating the degrees would have fewer decimal figures and be very convenient to remember.

When a liquid has a sp. gr. 1.2345, the number has four decimal figures. It would be much easier to read and to remember, if it is written 123.45.

(4) For the lighter liquids, the figures will become less, because we can write 23.45 instead of 0.2345.

(5) The same systems can be used throughout the heavier and lighter liquids.

EXAMPLES OF VARIOUS GRADUATIONS.

Substance	Usual hydrom.	Sp. gr.	New hydrom.
Benzene	. .	0.87907	87.907°
Petroleum	Baumé 45°	0.806	80.6°
Sulphuric acid	Baumé 45°	1.455	145.5°
Bromine	. .	3.1872	318.72°
Acetic acid	Tw. 9°	1.045	318.72°
Alcohol	(Vol % 5	0.9335	93.35°
Ammonia water	(15.4%)	0.942	94.2°

T. KAMOI.

TOKIO UNIVERSITY, JAPAN.
September 18, 1912.

THE EFFECT OF "LIME-SULPHUR" SPRAY MANUFACTURE ON THE EYESIGHT.—A NOTE.

Editor of the Journal of Industrial and Engineering Chemistry:

I have read, with a great deal of interest, the article in THIS JOURNAL, October, 1912, by Mr. James R. Withrow on "The Effect of Lime-sulphur Spray Manufacture on the Eyesight."

In making small batches of lime-sulphur spray in an uncovered kettle in the open air, we have experienced symptoms very similar to the ones noted, although no permanent blurring of the vision resulted. The eyelids, however, became very red and were badly swollen.

Since the trouble with the eyesight came only near the end of the "cook," and was very similar to the smarting sensation produced by getting the diluted spray in the eye, we supposed the disagreeable effects were caused by particles of solid material carried out with the escaping steam. No experiments were undertaken to prove this point.

The danger of permanent injury to the eyesight by the polysulphides of hydrogen—in case Mr. Withrow has at hand data to prove their existence in the escaping steam—should be clearly pointed out for the benefit of small fruit growers who make up their own lime-sulphur spray in uncovered kettles in batches ranging from one to five barrels.

ARCHIE J. WEITH.

DEPARTMENT OF INDUSTRIAL RESEARCH,
UNIVERSITY OF KANSAS,
LAWRENCE.

THE ANDREW CARNEGIE RESEARCH SCHOLARSHIP.

A Research Scholarship or Scholarships, of such value as may appear expedient to the Council of the Iron and Steel Institute from time to time, founded by Mr. Andrew Carnegie (Past-President), who has presented to the Iron and Steel Institute the sum of one hundred thousand dollars for the purpose, will be awarded annually, irrespective of sex or nationality, on the recommendation of the Council of the Institute. Candidates, who must be under thirty-five years of age, must apply

on a special form before the end of February to the Secretary of the Institute.

The object of this scheme of Scholarships is not to facilitate ordinary collegiate studies, but to enable students, who have passed through a college curriculum or have been trained in industrial establishments, to conduct researches in the metallurgy of iron and steel and allied subjects, with the view of aiding its advance or its application to industry. There is no restriction as to the place of research which may be selected, whether university, technical school, or works, provided it be properly equipped for the prosecution of metallurgical investigations.

The appointment to a Scholarship shall be for one year, but the Council may at their discretion renew the Scholarship for a further period instead of proceeding to a new election. The results of the research shall be communicated to the Iron and Steel Institute in the form of a Paper to be submitted to the Annual General Meeting of members, and if the Council consider the Paper to be of sufficient merit, the Andrew Carnegie Gold Medal shall be awarded to its author. Should the Paper in any year not be of sufficient merit, the Medal will not be awarded in that year.

By Order of the Council,

C. C. LLOYD, *Secretary.*

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

FIFTH ANNUAL MEETING.

The Annual Meeting of the Institute was held in Detroit, Michigan, December 4th to 7th, with headquarters at the Hotel Cadillac. In addition to routine business, the following program was presented:

Presidential Address: "Protection of Intellectual Property in Relation to Chemical Industry," *Dr. L. H. Baekeland.*
"Changing Rate of Setting Portland Cement," *Prof. E. E. Ware.*
"Industrial Efficiency," *Wm. M. Booth.*
"Technical Accounting and Chemical Control in Sugar Manufacture," *David L. Davoll, Jr.*
"Availability of Blast Furnace Slag as a Material for Making Brick," *Prof. A. E. White.*
"The Chemical Engineering Laboratory of Columbia University," *Prof. M. C. Whitaker.*
"Industrial Fellowships," *Prof. Robert K. Duncan.*
"Tests on the Opacity and Hiding Power of Pigments," *G. W. Thompson.*
"Composition of Glucose and Starch Sugars," *Dr. Edward Gudeman.*
"Solvents for Acetylene," *Prof. J. H. James.*
"Rotary Kiln Lining for Burning Portland Cement Clinker of Unusual Composition," *Chas. A. Newhall.*
"The Bituminous Rocks of the United States and their Use for Street Surfaces," *S. F. Peckham.*

Excursions were arranged to a number of chemical engineering plants and institutions in and around Detroit, including the following:

Parke Davis & Co.; Acme White Lead and Color Co.; Ford Motor Co.; Pennsylvania Salt Manufacturing Co.; Laboratories and Buildings of the University of Michigan (a complimentary luncheon was served at the University); Berry Bros., Ltd.; Detroit Sulphite Fibre Co.; Detroit Copper and Brass Rolling Mills; Michigan Malleable Co.

A Subscription Dinner was served at the Hotel Cadillac, at 7.00 P.M., Friday, December 6th.

THE CHEMICAL SOCIETIES IN NEW YORK CITY.

PROGRAM OF MEETINGS FOR THE SEASON 1912-1913.

At a joint conference of the Chairmen and Secretaries of the New York Sections of the American Chemical Society, the American Electro-Chemical Society and the Society of Chemical Industry, a schedule of meetings was worked out for the season 1912-1913. This schedule includes, in addition to the regular monthly meetings, three joint meetings, one to be held under the auspices of each of the societies represented. The program as adopted is as follows:

American Chemical Society, October 11, 1912.
Society of Chemical Industry, October 25, 1912.
American Chemical Society, November 8, 1912.
Society of Chemical Industry, November 22, 1912.
Joint meeting, American Chemical Society, December 13, 1912.
American Chemical Society, January 10, 1913.
Society of Chemical Industry (Perkin Medal), January 24, 1913.
Joint meeting, American Electro-Chemical Society, February 7, 1913.
American Chemical Society, March 7, 1913.
Society of Chemical Industry, March 28, 1913.
Joint meeting, Society of Chemical Industry, April 25, 1913.
American Chemical Society, May 9, 1913.
Society of Chemical Industry, May 23, 1913.
American Chemical Society, June 6, 1913.

ON THE STARCH OF GLUTINOUS RICE AND ITS HYDROLYSIS BY DIASTASE.—A CORRECTION.

In my article printed under the above title in THIS JOURNAL, 4, 578, the second table on page 580 should read as follows:

Carbohydrate solution.	Solution taken, cc.	Minimum quantity of baryta water to precipitate the carbohydrate, cc.
1 per cent. potato starch solution, 100 cc. } 1 per cent. soluble starch solution, 1.0 cc. }	2.0	1.6
1 per cent. glutinous rice starch solution, 100 cc } 1 per cent. erythrodextrin solution, 1.0 cc. }	2.0	1.6
1 per cent. glutinous rice starch solution, 100 cc } 1 per cent. erythrodextrin solution, 2.0 cc. }	2.0	1.8
1 per cent. glutinous rice starch solution, 100 cc } 1 per cent. erythrodextrin solution, 5.0 cc. }	2.0	2.6

YOSHIO TANAKA.

BOOK REVIEWS

Paper Pulps from Various Forest Woods. Experimental Data and Specimens of Soda and Sulphite Pulps. Compiled by HENRY E. SURFACE, Chemical Engineer in Forest Products. Forest Products Laboratory Series. U. S. Department of Agriculture, Forest Service, Washington, 1912.

This little publication consists of some twenty-three pages of tabulated data with descriptive matter and fifty-five samples of sheeted pulp inserted as leaves in the booklet. On this account the edition was very limited and its distribution confined almost exclusively to the pulp and paper industry. "The purpose of the report is to show specimens of paper pulps made from a number of different woods, and to give the experimental data connected with their production." It is recognized that further work must be done before the availability and suitability

of a given pulp can be definitely shown. "The report does show the yields, qualities, and general characters of the pulps and the cooking conditions used to obtain these results." It seems apparent already, however, that a number of the woods can be used commercially under suitable conditions. The report covers some woods now used commercially to a slight extent. While the difficulty of reproducing real industrial conditions on a small scale is believed by the compiler to have mitigated against a favorable quality of pulp in some cases, yet it is very apparent that the results obtained are sufficiently interesting to completely justify the trouble of conducting these experiments for the last half dozen years or more. It seems to the reviewer that this at least is one government industrial chemical project which is of real service to the country as a whole as well as a given industry and at the same time can hardly be said to be unfair competition with existing consulting chemists on the one hand or guilty (as in some bureaus) of carrying on at the public expense investigation work which should properly be done by an abundantly able but "Tom Sawyer" like industry. This laboratory is to be congratulated also in avoiding the industrial criticism of not having shown avenues of profitable pulp manufacture or of having been too precipitate in so doing. With ample and tempting results in hand it has, instead, modestly but clearly stated results, furnished the data of the work as far as conducted and supplied samples of the product, and wisely indicated that definite statement of the probably profitable pulping woods must be withheld until at least more detailed investigation is had. The work, so far, is the first necessary step, namely possibility of pulping, yield and character of the pulp from a wide variety of possible sources.

The results are in the hands of those who are most likely to utilize them and so secure the results desired by the Forest Service. One point might be worth mentioning, namely, the case of pulps 40 and 41 made from longleaf pine. It has long been my expectation that this source is to be one of great importance in the future. Now that difficulties in details of the application of the soda process to this wood have been successfully overcome by proper modifications, there should be a growing tendency for the pulp industry to center in the south.

JAMES R. WITHROW.

The Metallography of Iron and Steel. By ALBERT SAUVEUR. $7\frac{1}{2} \times 10\frac{1}{2}$ in. 425 pp. Illustrated. Sauveur and Bolyston, Cambridge, Mass., 1912. Price, $6.00 postpaid.

In the preface, the author offers this book to those seeking self instruction in the metallography of iron and steel; to teachers and students as a textbook; to manufacturers and users of iron and steel—having given due weight to the practical side—to the general reader interested in the scientific or practical features of the subject, as the language is simple; to experts, hoping they will find something original and suggestive.

It is divided into twenty-four lessons which have been very carefully arranged and show much thought and study as to the correct way to present the subject to beginners. For anyone starting out to learn the practical metallography of iron and steel, this book will be an enormous help. To those who have already obtained some skill in metallographic work it will serve as a guide for methods and for future studies. And still the book will be found of deep interest to those already proficient in metallography, because it contains new ideas, old ideas in new form, and a certain amount of matter, the theory of which is still open to debate.

The arrangement of subject matter is good and starting with apparatus used by the author, it deals with pure metals, their structure and the effects of mechanical and heat treatment; wrought iron; low carbon steel; medium-high and high carbon steel; impurities in steel. Next it takes up the thermal critical points, their occurrence, causes and effects; cast steel; the mechanical treatment of steel, annealing, hardening and tempering; theories of hardening; cementation and case hardening; special steels, constitution, properties, treatment and uses; cast iron; malleable cast iron. Then, in brief, sets forth the constitution of metallic alloys; the equilibrium diagram of iron-carbon alloys and ends with the phase rule. There are two appendices, one dealing with manipulation and apparatus, embracing polishing and development of structure; mounting, and microscopes used by other workers; the other on the nomenclature of the microscopic constituents, covering the reports of Committee 53 of the International Association for Testing Materials, of which Professor Sauveur was a most efficient secretary.

One or two criticisms can be made. The first is in reference to the pages: each section is a lesson with separate pages and hence it is difficult to refer to any particular topic, for first the lesson has to be found and then the page. The section on "apparatus for the metallographic laboratory" and the first appendix on "manipulations and apparatus" ought to have been combined and perhaps somewhat shortened by direct reference to trade catalogues. In regard to the illustrations, most of the micrographs are excellent, but one or two might be omitted or replaced by better ones in a second edition, especially some which are not photomicrographs, but drawings. Again, some of the photomicrographs are reproductions of cuts and not of the original photographs and as such have in many cases lost much detail.

In regard to certain theories it would be useless to expect everyone to agree. Ewing and Rosenhain's theory of growth of grains in metals; that crystals grow from the freezing point to the critical range; that undisturbed cooling is a condition necessary for the ready growth of crystals; that in slow cooling austenite passes through the stages of martenite, troostite, sorbite into pearlite and so on: these are matters on which there is still a diversity of opinion.

In the section on metallic alloys, the omission of the second diagram showing limited solubility in the solid state is to be noted. Several sections stand out clearly, such as those on the theories of hardening, on tempering, on case hardening and on alloy steels; particularly that dealing with the heat treatment, all of which are exceptionally well written and wonderfully clear. It is very clearly shown that the subcarbide theory of Arnold is "scientifically untenable and lacks experimental support."

The book is a good one, will supply a decided want, and will be undoubtedly welcomed by all those interested in iron and steel either from the practical or theoretical standpoint.

WILLIAM CAMPBELL.

Analysis of Metallurgical and Engineering Materials. By HENRY WYSOR, B.S. L. 8vo., pp. 82. The Chemical Publishing Co., Easton, Pa. Price, $2.00.

This work is intended for the use of students in chemical laboratories, and consists of the description of methods of analysis of the various materials and products of metallurgical processes. To facilitate the making and preservation of notes on the various operations, the alternate pages are blank. The descriptions are clear and in sufficient detail for the ordinary student. The methods given are, as a rule, well selected, but there are several exceptions: for instance the Bismuthate method for manganese is not described, nor is the direct combustion method for carbon in steel given. On page 52 the use of 1/5 normal sulphuric acid is advised for determining the alkalinity of water. For ordinary waters the 1/100 normal is much better. On page 64 is given a description of the determination of the B. T. U.'s in coal by the Parr Calorimeter which is not usually considered as accurate as the Mahler Bomb Calorimeter.

The use of the book will probably save the time of the instructor and some labor on the part of the student.

ANDREW A. BLAIR.

NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian, Chemists' Club, New York.

Applied Chemistry; Elementary. By LEWIS B. ALLYN. 8vo., 127 pp. Ginn & Co., New York.

Boiler Explosions. By E. J. RIMMER. 8vo., 152 pp. Price, $1.00. Constable & Co., London.

Carbohydrates; The Simple, and the Glucosides. By E. FRANKLAND ARMSTRONG. 8vo., 171 pp. Price, $1.50. Longmans, Green & Co., New York.

Celluloid; Its Manufacture, Applications and Substitutes. Translation into English by MASSELON, ROBERTS AND CELLARD. 8vo., 376 pp. Price, $6.25. Chas. Griffin & Co., London.

Colloid Chemistry. By W. OSTWALD. 3rd edition. I. 8vo., 330 pp. $2.25. Theodor Steinkopff, Dresden. (German.)

Dyestuffs; The Tar. By W. BERSCH. 2nd edition. 8vo., 248 pp. Price, $1.50. A. Hartleben, Vienna. (German.)

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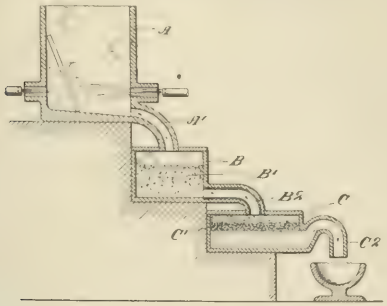
RECENT INVENTIONS

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

PROCESS OF REFINING COPPER.

U. S. Patent No. 1,037,538, to Walter S. Rockey and Hilliary Eldridge, assignors to Metallurgical Research Company.

The copper is first fused by exposing it to the direct heat of a furnace so as to melt the copper as rapidly as possible, regardless of its contamination by the furnace gases and the atmos-

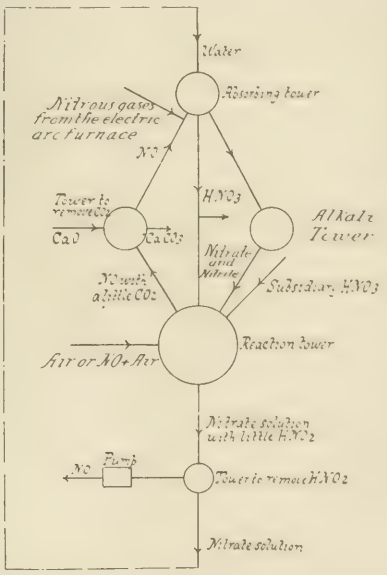


phere, the contamination being afterward removed by flowing the copper, before casting, into intimate contact with carbon, and preferably, first into contact with carbon and then into and through and under a flux, such as a flux of anhydrous boron trioxid (B_2O_3) or one containing anhydrous boron trioxid, and afterward leading the copper into suitable molds or a ladle.

PROCESS OF MAKING NITRATES AND NITRIC ACID.

U. S. Patent No. 1,039,325, to Otto Schönherr and Johannes Brode, assignors, to Norsk Hydro-Elektrisk Kvaelstofaktieselskab, of Christiania, Norway.

The patentees produce commercially pure nitrates from nitrites in a more advantageous manner by acting on such ni-

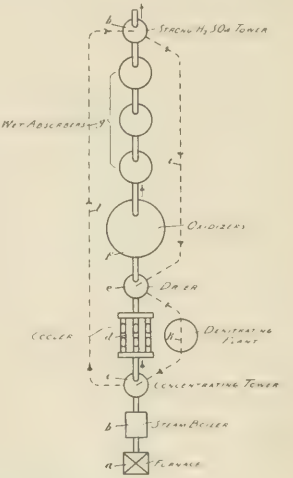


trites with nitric acid, then adding to the gases which are evolved so much oxygen that the atomic proportion of total oxygen present is to the quantity of combined nitrogen, as 5 is to 2, or thereabout, and then subjecting these gases to the absorbing action of water, or absorbing agent containing water but containing no basic compound. In this way nitric acid is obtained and can be used in the further treatment of a fresh quantity of nitrite. The gases which are obtained by treating nitrites with nitric acid, on being mixed with such quantities of oxygen, or oxygen-containing gases contain such proportion of the higher oxids of nitrogen that their absorption requires comparatively small apparatus.

PROCESS OF ABSORBING NITROUS GASES.

U. S. Patent No. 1,037,977, to Harry Pauling, assignor to Salpetersaure-Industrie-Gesellschaft, of Gelsenkirchen, Germany.

In the manufacture of nitric acid it is not possible to quantitatively absorb nitrogen oxides in water, a part of the NO_2 being decomposed in the absorption process into NO, which is only slightly soluble in water.



The patentee has discovered that nitrous gases can be quantitatively absorbed to form nitric acid if the unabsorbed nitrous gases which leave the wet absorbing apparatus proper, after being suitably oxidized, are taken up by sulphuric acid.

In the apparatus illustrated, nitrous gases produced in the apparatus *a*, an electric furnace for example, deliver the greater part of their heat to the boiler *b* and enter at a temperature of 400° C. or more into the acid-proof tower *c*. Here the gases absorb moisture from dilute sulphuric acid moving in a countercurrent, so that they become strongly charged with moisture. It is necessary to remove this moisture from the gases and this is partially done in the condensing or cooling plant *d* connected with the tower *c*. The gases are then further dried in the drying tower *e*. In this tower the gases are brought into intimate contact with concentrated sulphuric acid moving in a countercurrent so that they are dried, whereupon they are first oxidized in the tower *f* as by treatment with air or otherwise, and are then subjected in the towers *g* to a wet absorption. The remaining nitrogen oxids in the gases issuing from the towers *g* are entirely absorbed by highly concentrated sulphuric acid in the tower *h*.

The sulphuric acid leaving the lower end of the tower *h* in which the remaining oxids are absorbed by highly concentrated sulphuric acid contains compounds of nitrogen oxids with sulphuric acid, such as nitrosyl sulphuric acid, and is conducted by the pipe *i* to the drying tower *e*, where it takes up the moisture contained in the gases moving in a countercurrent thereto and is consequently diluted and more or less completely denitrated. From there the dilute sulphuric acid may pass through a small denitration plant, *k*, to the concentrating tower *c*, in which it is concentrated and then conducted back by the pipe *i* to the tower *h*, where the circulation begins again.

MARKET REPORT.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF NOVEMBER.

ORGANIC CHEMICALS.

Acetanilid	Lb.	20½	@	23
Acetone (drums)	Lb.	16½	@	17½
Alcohol, grain (188 proof)	Gal.	2.55	@	2.57
Alcohol, wood (95 per cent.)	Gal.	50	@	52
Alcohol, denatured (180 proof)	Gal.	40	@	42
Amyl Acetate	Gal.	2.65	@	2.85
Acetic Acid (28 per cent.)	C.	2.00	@	2.15
Aniline Oil	Lb.	10¾	@	11½
Benzoic Acid	Lb.	23	@	27
Carbon Tetrachloride (drums)	Lb.	10	@	11
Carbon Bisulphide	Lb.	11	@	12
Chloroform	Lb.	20	@	30
Carbolic Acid (drums)	Lb.	14	@	15
Citric Acid (domestic), crystals	Lb.	38½	@	39
Camphor (refined in bulk)	Lb.	44	@	—
Dextrine (imported potato)	Lb.	6	@	7
Dextrine (corn)	C.	3.00	@	—
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	19	@	20
Oxalic Acid	Lb.	8	@	8¾
Pyrogallic Acid (bulk)	Lb.	1.35	@	1.45
Salicylic Acid	Lb.	31	@	33
Starch (corn)	C.	2.10	@	2.21
Starch (potato)	Lb.	5¼	@	5¾
Tannic Acid (commercial)	Lb.	35	@	35½
Tartaric Acid crystals	Lb.	30¼	@	31

INORGANIC CHEMICALS.

Acetate of Lime (gray)	C.	2.50	@	2.60
Acetate of Lead (brown, broken)	Lb.	7¾	@	8
Alum (lump)	C.	1.75	@	2.00
Ammonium Carbonate, domestic	Lb.	8	@	8½
Ammonium Chloride, gray	Lb.	5⅞	@	6
Aluminum Sulphate	C.	90	@	1.75
Aqua Ammonia (drums) 16°	Lb.	2¼	@	2½
Arsenic, white	Lb.	5	@	5¼
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Barium Chloride	C.	1.40	@	1.55
Barium Nitrate	Lb.	4¾	@	5
Borax, crystals (bags)	Lb.	3¾	@	4¼
Boric Acid, crystals (powd.)	Lb.	7	@	7½
Bromine, bulk	Lb.	25	@	30
Bleaching Powder (35 per cent.)	C.	1.30	@	1.50
Barytes (prime white, foreign)	Ton	18.50	@	22.50
Blue Vitriol	Lb.	5½	@	5¾
Calcium Chloride	C.	65	@	90
Chalk (light precipitated)	Lb.	4	@	5
China Clay (imported)	Ton	11.50	@	18.00
Feldspar	Ton	7.00	@	9.00
Fuller's Earth, powdered	C.	80	@	85
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1.15	@	1.55
Iodine (resublimed)	Lb.	3.05	@	3.10
Lead Nitrate	Lb.	8¼	@	8¾
Lithium Carbonate	Lb.	65	@	70
Magnesite (raw)	Ton	7.50	@	8.50
Nitric Acid, 36°	Lb.	3⅞	@	4¼
Phosphorus	Lb.	35	@	90
Phosphoric Acid, sp. gr. 1.75	Lb.	22	@	26
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bromide	Lb.	35	@	37
Potassium Permanganate (bulk)	Lb.	9¾	@	10
Potassium Cyanide (bulk) 98–99%	Lb.	19	@	24
Potassium Iodide (bulk)	Lb.	2.60	@	2.65
Potassium Chlorate, crystals	Lb.	8¼	@	9½
Potassium Nitrate (crude)	Lb.	5	@	5⅛
Potassium Bichromate, 50°	Lb.	6⅞	@	7
Quicksilver, Flask		41.00	@	42.00
Salt Cake (glass-makers')	C.	55	@	65
Silver Nitrate	Oz.	39⅞	@	40⅞
Soapstone in bags	Ton	10.00	@	12.00
Sodium Acetate	Lb.	4¼	@	5
Sodium Chlorate	Lb.	8¼	@	9½
Sodium Bicarbonate (English)	Lb.	2¾	@	3
Sodium Bichromate	Lb.	5⅛	@	5¼
Sodium Hydroxide, 60 per cent	C.	1.60	@	1.65
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent., spot	C.	2.60	@	—
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	6⅞	@	7⅝
Sulphur, Roll	C.	1.85	@	2.15
Sulphur, Flowers (sublimed)	C.	2.20	@	2.60
Sulphuric Acid, 60° B.	C.	85	@	1.00
Talc (American)	Ton	15.00	@	20.00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	14¼	@	14½
Tin Oxide	Lb.	52	@	54
Zinc Chloride (granulated)	Lb.	4¼	@	4½
Zinc Sulphate	Lb.	2¼	@	2½

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	40	@	44
Black Mineral Oil, 29 gravity	Gal.	12	@	12½
Castor Oil (No. 3)	Lb.	9½	@	10½
Ceresin (yellow)	Lb.	10	@	15
Corn Oil	C.	5.55	@	5.60
Cottonseed Oil (crude), f. o. b. mill	Gal.	36½	@	38
Cylinder Oil (light, filtered)	Gal.	19½	@	20
Japan Wax	Lb.	9¾	@	10¼
Lard Oil (prime winter)	Gal.	88	@	93
Linseed Oil (double-boiled)	Gal.	57	@	60
Paraffine Oil (high viscosity)	Gal.	25½	@	26
Paraffine (crude 120 & 122 m. p.)	Lb.	3¼	@	3¾
Rosin Oil (first run)	Gal.	36	@	37
Spindle Oil, No. 1	Gal.	16	@	16½
Sperm Oil (bleached winter), 38°	Gal.	72	@	74
Stearic Acid (double-pressed)	Lb.	9½	@	10¼
Tallow (acidless)	Gal.	65	@	68
Tar Oil (distilled)	Gal.	30	@	31

METALS.

Aluminum (No. 1 ingots)	Lb.	27	@	27½
Antimony (Hallet's)	Lb.	9⅝	@	10½
Bismuth (New York)	Lb.	2.10	@	2.15
Copper (electrolytic)	Lb.	17.40	@	17.60
Copper (lake)	Lb.	17⅝	@	17¾
Lead, N. Y.	Lb.	4.75		
Nickel	Lb.	50	@	55
Platinum (refined)	Oz.	46.35	@	47.00
Silver	Oz.	62⅝		
Tin	Lb.	50	@	—
Zinc	Lb.	7.40	@	7.50

FERTILIZER MATERIALS.

Ammonium Sulphate	C.	3.18	@	3.20
Fish Scrap, domestic, dried	Unit	2.75	&	10
Blood, dried	Unit	2.70	@	2.75
Tankage, high grade	Unit	2.65	&	10
Bone, 4½ and 50, ground, raw	Ton	28.50	@	—
Potassium, "muriate," basis 80%	Ton	38.55	@	—
Phosphate, acid, 16 per cent	Ton	6.75	@	7.00
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent	Ton	3.70	@	3.80
Tennessee, 68–72 per cent	Ton	4.25	@	4.50
Pyrites, furnace size, imported	Unit	0.13¼	@	0.13½
Castor meal	Unit	2.60	@	—
Mowrah meal	Ton	8.50	@	9.00

AUTHOR INDEX

THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY

VOL. IV, 1912

ACHESON, E. S. Deflocculation Address 62
ADAMS, A. B. The Distillation of Alcohol 8
ADAMS, A. B. and J. M. DORAN. Some Data on the Manufacture of Smoking Opium and its Chemical Composition 429
ADAMS, G. O. and H. W. CLARK. The Influence of Carbon upon Nitrification 272
ALLEN, L. C. and W. A. JACOBS. An Electric Still Adapted for Difficult Distillations 118
ALMY, C., JR. and W. K. LEWIS. Factors Determining the Capacity of a Filter Press 528
ARCHIBALD, E. H. and J. N. LAWRENCE. The Determination of Moisture in Coals 258
ARTHUR, W. and W. H. WALKER. Galvanized Structure of Iron 397

BAEKELAND, L. H. Morris Loeb (Ed.) 784
BAEKELAND, L. H. Phenol-Formaldehyde Condensation Products 737
BAEKELAND, L. H. Phenol Formaldehyde Condensation Products. A Correction 857
BAEKELAND, L. H. The Abuses of Our Patent System (Patent Symposium) 333
BAEKELAND, L. H. The Incongruities of American Patent Litigation (Ed.) 785
BAILEY, E. G. Introduction to the Study of Fuel, by F. J. Brislee (Book Review) 626
BANCROFT, W. D. Physical Industrial Chemistry (Ed.) 79
BARR, W. M. and R. E. BUCHANAN. The Production of Excessive Hydrogen Sulfid in Sewage Disposal Plants and Consequent Disintegration of the Concrete 564
BASKERVILLE, C. Extraction of Thoria 821
BASKERVILLE, C. Morris Loeb (Obituary 846
BASKERVILLE, C. and W. A. HAMOR. The Chemistry of Anaesthetics, IV: Chloroform 212, 278, 362, 422, 499, 571
BASKERVILLE, C. and H. S. REIDERER. The Chlorides of Carbon as Solvents, I. Carbon Tetrachloride 645
BASSETT, W. H. Need of Special Alloys for Special Purposes (Mineral Wastes Symposium) 167
BASSETT, W. H. Zinc Losses (Mineral Wastes Symposium) 164
BEATTIE, J. H. and J. J. SKINNER. An Examination of City Street Sweepings 604
BENNER, R. C. An Electric Laboratory Furnace 43
BENNER, R. C. The Need of Chemical Control in Furnace Operation 691
BENSON, H. K. Design and Equipment of the Chemical Engineering Laboratory at the University of Washington 609
BERNTHSEN, H. A. Synthetic Ammonia 760
BEROLZHEIMER, D. D. New Publications 70, 156, 234, 314, 391, 474, 551, 628, 700, 779, 859, 920
BEROLZHEIMER, D. D. Papers of Special Interest to Industrial Chemists and Chemical Engineers from the Proceedings of the Eighth International Congress of Applied Chemistry 779
BEROLZHEIMER, D. D. Recent Journal Articles Classified List 71, 156, 235, 314, 392, 474, 551, 629, 701, 781, 859, 920
BEROLZHEIMER, D. D. Transactions of the American Institute of Chemical Engineers, Vol. III (1910) Book Review 313
BIDTEL, E. Valuation of Fluorspar 201
BIDTEL, E. Valuation of Fluorspar. A Correction 348
BLAIR, A. A. Analysis of Metallurgical and Engineering Materials by Henry Wysor (Book Review) 919
BLASDALE, W. C. An Improved Extraction Apparatus 302
BLEININGER, A. V. The Relation of the Silicate Industries to Conservation (Mineral Wastes Symposium) 180
BOECK, P. A. Notes on a New Form of Extraction Thimble 303
BOECK, P. A. and M. A. WILLIAMSON. A New Type of Inorganic Filter for Laboratory Purposes 672
BOGERT, M. T. American Commission on Organic Nomenclature 309
BORROWMAN, G. Some Observations on the Disintegration of Concrete Cinder 405
BOSWELL, M. C. and J. I. GOODFRIHAM. The Composition of Fusel Oil from Beet Molasses 667
BOWSER, L. T. Carbon Dioxide. Its Volumetric Determination 203
BOWSER, L. T. On the Determination of Carbon Dioxide in Soils 265
BOYLE, J. J. Determination of Manganese in Steel 202
BRADLEY, C. E. and H. V. TARTAR. A Comparative Study of Methods for the Determination of Hard and Total Soft Resins in the Hop 209
BRADLEY, C. E. and H. V. TARTAR. The Ripening of Hops 591
BRADLEY, L. The Electrical Precipitation of Suspended Particles by the Cottrell Processes 908
BRADY, WM. Metallurgy of Iron and Steel, by B. Stoughton (Book Review) 390
BRECKENRIDGE, J. E. Committee on Potash, Fertilizer Division 224
BRECKENRIDGE, J. E. Division of Forty-fifth Meeting A. C. S. Fertilizer Chemists 151
BRECKENRIDGE, J. E. The Manufacture of Chemical Manure, by J. Fritsch (Book Review) 233
BROEMAN, F. C. Method for Determining Fat in Sugared Evaporated Milk 672
BROGDON, J. S. The Analyst *vs.* the Chemist 684
BROWNE, C. A. Cocoa and Chocolate, their Chemistry and Manufacture, by R. Whymper (Book Review) 473
BROWNE, C. A. Handboek ten Dienste van de Suikerrietcultur en de Reitsuikerfabricage op Java, by Geerligs, C. P. (Book Review) 69
BROWNE, C. A. The Chemistry of Breadmaking, by James Grant (Book Review) 550
BROWNE, C. A. The Technology of Bread-making, etc., by W. Jago and W. C. Jago (Book Review) 313
BROWNE, C. A. Vinegars and Catsup, Interpretation of Standards, Analyses, Etc., by R. O. Brooks (Book Review) 628
BROWNE, L. A. An Improved Method of Assay for Aromatic Sulfuric Acid 512
BROWN, O. W. and A. R. NEES. A Study of the Variations of the Physical and Chemical Properties of Red Lead 867
BRUBAKER, H. W. A New Apparatus for the Volumetric Determination of Carbon Dioxide 599
BUCHANAN, R. E. and W. M. BARR. The Production of Excessive Hydrogen Sulfid in Sewage Disposal Plants and Consequent Disintegration of the Concrete 564
BURRELL, G. A. Natural Gas Investigations of the Bureau of Mines 614
BURRELL, G. A. New Forms of Gas Analysis Apparatus 297
BURRELL, G. A. The Composition of Some Mine Gases and a Description of a Simple Methane Apparatus 96

CABOT, S. The Phenomenon of the Apparent Disappearance of the Higher Boiling Phenols in Creosoted Wood and its Explanation 266
CABOT, S. The Value of the Higher Phenols in Wood-Preserving Oils 206
CAIN, J. R. The Determination of Chromium and its Separation from Vanadium in Steels 17
CAIN, J. R. and D. J. DEMOREST. A New Method for the Determination of Vanadium: An Explanation 256
CAIN, J. R. and J. C. HOSTETTER. A Rapid Method for the Determination of Vanadium in Steels, Ores, etc., Based on its Quantitative Inclusion by the Phosphomolybdate Precipitate 250
CAMERON, F. K. Potash from the Pacific Kelps (Ed.) 76
CAMERON, F. K. Seaweed, Potash and Iodine 690
CAMERON, F. K. Waste and Conservation of Phosphoric Acid and Potash (Mineral Wastes Symposium) 169
CAMPBELL, W. The Metallography of Iron and Steel, by Albert Sauveur (Book Review) 919
CARPENTER, F. B. Committee on Fertilizer Legislation. Division Report 223
CARPENTER, F. B. Fertilizer and Fertilizer Hints, by J. E. Halligan Book Review) 472
CARPENTER, F. B. Plant Food: Its Sources, Conservation, Preparation and Application, by W. K. Bowker (Book Review) 234
CARPENTER, L. L. and G. RIES. The Stormer Viscosimeter and the Value of Viscosity Determinations by its Use 901
CARY CURRY, H. I. The Underwriters' Laboratories Extraction Apparatus 535
CHANDLER, C. F. Presentation Address. Perkin Medal Award 132
CHAPIN, H. C. A Modified Victor Meyer Apparatus 684
CHAPIN, H. C. Two Pieces of Laboratory Apparatus 453
CHENEY, L. B. and G. W. PATTERSON. Contact Sulphuric Acid from Brimstone 723
CLARK, H. W. and G. O. ADAMS. The Influence of Carbon upon Nitrification 272
CLARKSON, P. S. The Development of Hydrosulphites in their Relation to Modern Dyestuffs 733
COGGESHALL, G. W. and A. S. CUSHMAN. The Production of Available Potash from the Natural Silicates 821

COLLINS, A. F. A Method for Assaying Spirits of Camphor 514
COLLISON, R. C. Inorganic Phosphorus in Plant Substances. A Method of Estimation 606
COLWELL, J. V. V. Frederick J. Mayer (Obituary) 777
CONRADSON, P. H. Apparatus and Method for Carbon Test and Ash Residue in Petroleum Lubricating Oils 903
CONRADSON, P. H. Apparatus and Method for Sulfur Determination in Petroleum Illuminating and Lubricating Oils 842
CONRADSON, P. H. Apparatus for the Examination and Study of the Behavior of Valve and Cylinder and other Petroleum Lubricating Oils, in Saturated and Superheated Steam, Carbon Dioxide, Air and Other Gases 744
COOLIDGE, W. D. Some Applications of Wrought Tungsten and Molybdenum (Ed.) 2
COTTRELL, F. G. Mineral Losses in Gases and Fumes (Mineral Wastes Symposium) 182
COTTRELL, F. G. The Research Corporation, an Experiment in Public Administration of Patent Rights (Ed.) 864
CROSSLEY, T. L. A Simple Form of Laboratory Support 846
CRUESS, W. V. The Effect of Sulfurous Acid on Fermentation Organisms 581
CURRY, B. E. and T. O. SMITH. A Short Method for the Determination of Soluble Arsenic in Commercial Lead Arsenates 198
CUSHMAN, A. S. Notes on a Study of the Temperature Gradients of Setting Portland Cement 728
CUSHMAN, A. S. and G. W. COGGESHALL. The Production of Available Potash from the Natural Silicates 821
CUTLER, D. A. Organization of Rubber Section, American Chemical Society 547

DAVIS, L. and A. G. WOODMAN. The Determination of Benzaldehyde in Maraschino Cherries and Maraschino Liqueur 588
DAY, A. L. and R. B. SOSMAN. The Expansion Coefficient of Graphite 490
DEMOREST, D. J. A New Method for the Determination of Vanadium 249
DEMOREST, D. J. The Bismuthate Method for Manganese 19
DEMOREST, D. J. The Determination of Chromium and Vanadium in Steel 895
DEMOREST, D. J. and J. R. CAIN. A New Method for the Determination of Vanadium: An Explanation 256
DENIS, W. and O. FOLIN. A New Colorimetric Method for the Determination of Vanillin in Flavoring Extracts 670
DENNIS, L. M. A New Form of Orsat Apparatus 898
DENNIS, L. M. and W. J. O'BRIEN. The Determination of Phosphorus in Commercial Acetylene 834
DEWEY, F. P. The Business Aspect of the Kelp Proposition 311
DEWEY, F. P. The Direct Determination of Small Amounts of Platinum in Ores and Bullion 257
DICKSON, W. S. and C. H. HERTY. The Resenes of Resins and Oleoresins 495
DODGE, F. D. The Determination of Eucalyptol (Cineol) in Essential Oils 592
DORAN, J. M. A Simple Test for the Determination of Butter Fat in Butter 841
DORAN, J. M. and A. B. ADAMS. Some Data on the Manufacture of Smoking Opium and its Chemical Composition 429
DOWZARD, E. A Laboratory Generator for Hydrochloric Acid Gas 452
DUCCA, W. A. Testing Methods of Rubber Contents in Raw and Vulcanized Rubber 372
DUISBERG, CARL. The Latest Achievements and Problems of the Chemical Industry 749
DAY, A. L. and R. B. SOSMAN. The Expansion Coefficient of Graphite 490

ELDRED, F. R. Division of Pharmaceutical Chemistry, Forty-fifth Meeting A. C. S. 150
ELDRED, F. R. The Scope of Pharmaceutical Chemistry 396
EMERSON, H. W. and E. R. WEIDLEIN. Jamaica Camphor 33
EMERY, W. O. The Volatile Acidity of Gum Tragacanth Compared with that of Indian Gum 374
ERNST, W. A. A Substitute for the Blast Lamp 221
EVANS, W. W. The Chemistry of Rubber Industry, by H. E. Potts (Book Review) 627
EYDE, SAMUEL. Oxidation of Atmospheric Nitrogen and Development of Resulting Industries in Norway. Address 771

FAIRCHILD, J. G. The Accurate Volumetric Determination of Phosphoric acid in Phosphate Rock 520
FAIRLIE, D. M. and J. N. PRING. The Synthesis of Hydrocarbons at High Temperatures and Pressures 812
FELDSTEIN, L. The Refractive Index of Beeswax 498
FERGUSON, W. C. A Plan for Organized Research and Analytical Chemistry in Successful Chemical Manufacturing 905
FINK, C. G. Die Metallurgie des Wolframs mit besonderer Berueck sichtigung der Elektrometallurgie, by Mennicke, Dr. Hans 70
FLEMING, R. S. Notes on the Composition and Analysis of Desiccated Milk and Cream 543
FLEMING, W. R. Corrosion of Iron in Pure Water and Air Combined. The Electrolytic Theory Again Confirmed 480
FOLIN, O. and W. DENIS. A New Colorimetric Method for the Determination of Vanillin in Flavoring Extracts 670
FOOTE, H. W. and S. R. SCHOLES. The Extraction of Potash and Alumina from Feldspar 377
FORBES, E. B. Alundum not Constant in Weight 544
FOX, C. P. Apocynum or Indian Hemp Rubber 387
FOX, C. P. Perilla Oil 229
FRAPS, G. S. Relation of Active Potash to Pot Experiments 525
FRASCH, HERMAN. Address of Acceptance (Perkin Medal Award) 134
FRERICHS, F. W. A Note 69
FRERICHS, F. W. Manufacture and Testing of Shipping Cylinders for Anhydrous Ammonia (Address) 80
FRERICHS, F. W. The Manufacture of Chloroform from Bleaching Powder and Ethyl Alcohol 345, 406

GAINES, R. H. Monel Metal 354
GAITHER, E. W. A New Apparatus for the Determination of Carbon Dioxide 611
GALLAGHER, F. E. Division of Industrial Chemists and Chemical Engineers, Forty-fifth Meeting A. C. S. 148
GARRATT, F. The Rapid Determination of Vanadium in Steel 256
GEER, W. C. Rubber, by P. Schidrowitz (Book Review) 389
GEERLIGS, C. P. Handboek ten Dienste van de Suikerrietcultur en de Reitsuikerfabricage op Java, by C. A. Browne (Book Review) 69
GOODERHAM, J. L. and M. C. BOSWELL. The Composition of Fusel Oil from Beet Molasses 667
GORTNER, R. A. and C. O. ROST. The Determination of Total Manganese in Soils 522
GROSVENOR, W. M. The U. S. Patent System (Ed.) 318

HADLOCK, W. L. An Improvement on the Kjeldahl Distilling Apparatus 222
HALL, E. J. A Manual of Fire Assaying, by C. H. Fulton (Book Review) 473
HALL, W. E. Addresses to Engineering Students by various speakers (Book Review) 155
HAMOR, W. A. Current Industrial News 307, 382, 459, 539, 619, 686, 774, 849, 913
HAMOR, W. A. The Purification and Softening of Water by Permutite (Ed.) 240
HAMOR, W. A. Technologic Papers of the Bureau of Standards No. 3; Tests of the Absorptive and Permeable Properties of Portland Cement Mortars and Concretes, together with Tests of Dampproofing and Waterproofing Compounds and Materials, by Wig and Bates (Book Review) 549
HAMOR, W. A. The Third International Rubber Exhibition 855
HAMOR, W. A. and C. BASKERVILLE. The Chemistry of Anaesthetics, IV; Chloroform 212, 278, 362, 422, 499, 571
HANSON, H. Maine Section of the American Chemical Society 546
HARDING, E. P. and L. L. NYE. A Rapid Control Method for the Determination of Oil in Grains 895
HART, E. Alumina, Silica and Potash from Feldspar 827
HART, E. Laboratory Generator for Hydrochloric Acid Gas. A Note 626
HART, E. Potash, Silica and Alumina from Feldspar 827
HARTWELL, B. L. and F. R. PEMBER. The Effect of the "Wet Process" on the Availability of Low-grade Nitrogenous Materials 441
HAWLEY, L. F. and R. C. PALMER. Distillation of Resinous Wood by Saturated Steam 789
HEATH, G. L. The Estimation of Oxygen and Occluded Gases in Copper, Etc. (Author's Note) 691
HEATH, G. L. The Estimation of Oxygen and Occluded Gases in Copper and a Correction to the Electrolytic Assay in the Complete Analysis of Copper 402
HELLMAN, C. G. A Colorimetric Method for the Determination of Carbon in Iron and Steel. A Note 548
HERSTEIN, B. Patents and Chemical Industry in the United States (Patent Symposium) 328
HERTY, C. H. and W. S. DICKSON. The Resenes of Resins and Oleoresins 495
HILLEBRAND, W. F. Snap Commercial Analysis, by F. W. Babington (Book Review) 700
HIRSCH, A. The Preparation and Properties of Metallic Cerium. A Correction 65
HIRSCH, A. The Production of Ethyl Alcohol from Waste Products (Ed.) 478
HIRST, C. T. and R. STEWART. Comparative Value of Irrigated and Dry-farming Wheat for Flour Production 270
HOLMES, J. A. Carbon Wastes (Mineral Wastes Symposium) 160
HORNE, W. D. Temperature Corrections in Raw Sugar Polarizations 41
HOSTETTER, J. C. and J. R. CAIN. A Rapid Method for the Determination of Vanadium in Steels, Ores, Etc., Based on its Quantitative Inclusion by the Phosphomolybdate Precipitate 250

HUBBARD, W. S. Difficulties in the Colorimetric Estimation of Vanillin.. 669
HUGHES, L. S. A Method for the Utilization of Lead Furnace Fume 262

JACKSON, C. L. Wolcott Gibbs (Letter to Editor) 51
JACOBS, W. A. and I. C. ALLEN. An Electric Still Adapted for Difficult Distillations 118
JAGGARD, B. P. Chemistry and the Lithographic Industry 470
JESSE, R. H., JR. Some Tests on a New Calorimeter 748
JONES, C. H. Activity of Organic Nitrogen as Measured by the Alkaline Permanganate Method 438

KAMOI, T. The Graduation of Hydrometers (A Note) 917
KELLEY, W. P. and W. MCGEORGE. The Determination of Humus in Hawaiian Soil 664
KENNEDY, C. A Modification of the Sweeney Method for Crude Fiber 600
KICHLINE, F. O. The Determination of Carbon in Steel by Direct Combustion in the Newest Form of Shimer Crucible, with the Aid of a Perforated Clay Disc 683
KIEFER, H. E. Free Lime in Portland Cement 358
KNEFF, C. W. Sampling Cone 682
KNOTE, J. M. and W. R. WORK. A Modification of the Frary Electrodynamic Stirring Device 534
KNUDSEN, H. Seaweed, Potash and Iodine. A Criticism 623
KOBAYASHI, K. The Kambara Earth. A Decolorizing Material for Mineral Oils, Etc 891
KOENIG, W. A. Carbon Dioxide Absorption Bottle 844
KOHMAN, H. A. Salt Rising Bread and Some Comparisons with Bread made with Yeast 20, 100
KOHOUT, J. F. A Colorimetric Method for the Determination of Carbon in Iron and Steel 378
KRAUSS, V. P. Cobalt Driers 731
KRESS, O. Casein, Its Preparation and Technical Utilization, by Robert Scherer (Book Review) 391
KRESS, O. Researches in Cellulose, Vol. III, by Cross and Bevan (Book Review) 858

LANDRUM, R. D. Enamels for Sheet Steel 561
LANGMUIR, A. C. Committee on Professional Code of Ethics, Industrial Division 226
LAWRENCE, J. N. and E. H. ARCHIBALD. The Determination of Moisture in Coals 258
LEAVITT, S. Studies on Soil Humus 601
LEFFMANN, H. Detection of Formaldehyde in Foods 626
LENHER, V. Analyse der seltenen Erden und der Erdsäuren, Die, by Meyer and Hauser (Book Review) 858
LENHER, V. Contamination of Laboratory Samples by Iron Derived from Crushing Machinery 471
LEVINSON, S. Some Practical Methods for Testing and Identifying Colors for Printing Inks and Similar Pigments 661
LEWIS, W. K. and C. ALMY, JR. Factors Determining the Capacity of a Filter Press 528
LINDER, W. V. Soy Bean Cheese 897
LIPMAN, C. B. The Effect of Ignition on the Solubility of Soil Phosphates 663
LITTLE, A. D. The Abuse of Brand (Mineral Wastes Symposium) 178
LOMANITZ, S. The Oil of Pochote 625
LONGMANS, GREEN & Co. Dictionary of Applied Chemistry. A Correction, by E. Thorpe (Book Review) 698
LLOYD, C. C. Research Scholarship, The Andrew Carnegie Announcement 917
LUCAS, CAPT. A. F. Geology of the Sulphur and Sulphur Oil Deposits of the Coastal Plain (Perkin Medal Award) (Address) 140
LUCKE, C. E. Fuel Economy in Factories (Address) 58

MACNIDER, G. M. A Method for Determining the Value of Commercial Starches for Use in Cotton Mills 417
MARRS, L. E. Annual Tables of Constants and Numerical Data, Chemical, Physical and Technological, by International Commission of Seventh International Congress (Book Review) 627
MASON, C. D. Ordinary Writing Fluid for Marking Porcelain Crucibles. A Note 691
MASON, G. F. Division of Food and Agricultural Chemistry. Forty-fifth Annual Meeting A. C. S. 149
MAY, C. E. and C. P. SHERWIN. Concerning the Sugar Content of Watermelons 585
MAYWALD, F. J. Meeting of the Rubber Section. Forty-fifth Meeting A. C. S. 152
MCGEORGE W. The Occurrence of Efflorescence on Lava Bricks 559
MCGEORGE W. and W. P. KELLEY. The Determination of Humus in Hawaiian Soil 664
MCILHINEY, P. C. A Method of Examining China Wood Oil 496
MCILHINEY, P. C. Die Chemie der trocknenden Oele, by W. Fahrion (Book Review) 313
MCILHINEY, P. C. German Varnish Making, by Max Bottler (Book Review) 628
MCKEE, R. H. A Still for Absolute Alcohol 46
MCKENNA, C. F. Hardness of Plasters and Cements, and a Simple Chronographic Apparatus for Recording Set 110
MCKENNA, C. F. Portland Cement, by R. K. Meade (Book Review) 698
MEADE, R. K. The Distribution of Power in Portland Cement Manufacture 378
MERSEBEAU, G. Die Polarimetric der Erdöle, by M. A. Rakusin (Book Review) 155
MESSEL, R. Progress in Industrial Chemistry 767
METZGER, F. J. Technical Methods of Chemical Analysis, by G. Lunge (Book Review) 472
METZGER, F. J. and F. W. ZONS. A Volumetric Method for the Determination of Thorium in the Presence of Other Rare Earths. The Analysis of Monazite Sand 493
MILFORD, L. R. Modified Bunsen Valve 845
MILFORD, L. R. Recent Analyses of the Saratoga Mineral Waters 593
MILFORD, L. R. The Determination of Lithium 595
MILLS, H. P. A Punch for Straight Rubber Test Pieces 452
MINOR, J. C., JR. The Manufacture and Testing of Carbonic Acid Cylinders 88
MITCHELL, T. A. Automatic Filter Feed 613
MOORE, H. C. Calculation of Sulfuric Acid Stock by Approximate *vs.* Accurate Methods. A Special Slide 677
MORK, H. S. Die Chemie der Cellulose with Particular Reference to the Textile and Cellulose Industries, by C. G. Schwalbe 472
MUNROE, C. E. Address at the Unveiling of the Bust of Wolcott Gibbs 48
MUNROE, C. E. Note on the Production of Mercury Fulminate 152
MUNROE, C. E. Report of the Delegate to the Joint Conference on the Patent System 466
MUNROE, C. E. The Present Status of Gas Industry and its Outlook 536

NEES, A. R. and O. W. BROWN. A Study of the Variations of the Physical and Chemical Properties of Red Lead 867
NITCHIE, C. C. A Rapid Determination of Sulfur in Roasted Blende 30
NORTON, T. H. Chemical Industries in Sweden (Consular Note) 51
NORTON, T. H. Chemical Industries of Norway (Consular Note) 691
NORTON, T. H. Improved Sulfuric Acid Chambers (Consular Note) 532
NOWAK, C. A. A Simple and Inexpensive Conductivity Cell 679
NYE, L. L. and E. P. HARDING. A Rapid Control Method for the Determination of Oil in Grains 895

O'BRIEN, W. J. and L. M. DENNIS. The Determination of Phosphorus in Commercial Acetylene 834
OLSON, GEO. A. Composition of Dry Gluten and its Relation to the Protein Content of Flour 206
O'NEILL, J. G. The Continuous Purification of Coal Gas with Weak Ammonia Liquor 876
OVITZ, F. K. and HORACE C. PORTER. Deterioration and Spontaneous Heating of Coal in Storage 5

PALMER, R. C. and L. F. HAWLEY. Distillation of Resinous Wood by Saturated Steam 789
PARKER, C. L. Recent Inventions 72, 157, 236, 315, 393, 475, 552, 629, 701, —, 860, 921
PARR, S. W. A New Alloy with Acid Resisting Properties 844
PARR, S. W. A New Calorimeter Bomb with Special Advantages as to Material of Construction and Method of Operation 746
PARR, S. W. The Causes for Variations in Volatile Matter Determinations 352
PARSONS, C. L. Miscellaneous Mineral Wastes (Mineral Wastes Symposium) 185
PARSONS, C. L. Mineral Wastes: The Chemists' Opportunity 125
PATCH, J. B. The End of the Coöperative Glass Factories in Italy 548
PATRICK, W. A. and W. H. WALKER. The Determination of Oxygen in Iron and Steel by Reduction in an Electric Vacuum Furnace 799
PATRICK, W. W. and G. C. WILSNACK. A New Volumetric Method for Tin 597
PATTEN, A. J. and C. S. ROBINSON. Neutral Ammonium Citrate Solution 443
PATTERSON, G. W. and L. B. CHENEY. Contact Sulfuric Acid from Brimstone 723
PEGRAM, G. B. The Chemistry of the Radio Elements, by F. Soddy (Book Review) 627
PEMBER, F. R. and B. L. HARTWELL. The Effect of the "Wet Process" on the Availability of Low Grade Nitrogenous Materials 441
PENCE, C. M. The Bromine and Iodometric Methods for the Volumetric Determination of Cresol 518
PENNOCK, JOHN D. Losses of Combined Nitrogen (Mineral Wastes Symposium) 172
PETER, A. M. Committee on Phosphate Rock. Fertilizer Division 225

PILKINGTON, B. and H. V. TARTAR. The Effect of Kiln Drying at 145° F. on the Composition of the Hop 839

POLENSKE, PAUL. The Chlorine Content of Milk 48

PORTER, F. B. A Method for Testing out Problems in Acid Phosphate Manufacture 264

PORTER, H. C. and F. K. OVITZ. Deterioration and Spontaneous Heating of Coal in Storage 3

POUGH, F. H. Sulfur Mines of the Union Sulphur Company in Louisiana (Perkin Medal Award) (Address 143

PRATT, D. S. A New Melting Point Apparatus 47

PRICE, A. F. Thomas Price (Obituary) 917

PRICE, W. B. The Technical Analysis of Brass and the Non-ferrous Alloys, by Price and Meade (Author's Note on Book Review) 469

PRING, J. N. and D. M. FAIRLIE. The Synthesis of Hydrocarbons at High Temperatures and Pressures 812

PRITCHARD, T. W. Some Recent Developments in Wood Distillation 338

PUTT, E. B. Micro Chemical Tests for the Identification of Some of the Alkaloids 508

RAFSKY, H. R. and E. SUTERMEISTER. On the Quantitative Estimation of Sodium Hydroxide in Black Liquor 568

RAUTENSTRAUCH, W. Strength of Materials, by Slocum and Hancock (Book Review) 471

REDMAN, L. V. and E. O. RHODES. Rapid and Accurate Methods for Determining Phenol 655

REDMOND, N. G. A Modification of the Babcock Test as Applied to the Estimation of Fat in Desiccated Milk 544

REMINGTON, J. P. Progress of the Work on the Revision of the U. S. Pharmacopoeia 457

RHODES, E. O. and L. V. REDMAN. Rapid and Accurate Methods for Determining Phenol 655

RHODES, F. H. The Detection and Determination of Cyanogen and Hydrogen Cyanide 652

RICE, E. W. Laboratory Preparation of Litmus Paper 229

RICE, G. S. Description of the Explosion Test at the Experimental Mine of the U. S. Bureau of Mines, Feb. 24, 1912 488

RICHARDS, T. W. The Control of Temperature in the Operations of Analytical Chemistry 910

RICHARDSON, C. Committee on Definition of Industrial Terms. Industrial Division Report 226

RICHARDSON, W. D. Chemiker Kalender. By Rudolf Biedermann (Book Review) 472

RICHARDSON, W. D. The Méker Burner 66

RICHARDSON, W. D. and E. F. SCHERUBEL. A Modified Wiley Extraction Apparatus 220

RIEDERER H. S. and C. BASKERVILLE. The Chlorides of Carbon as Solvents. I. Carbon Tetrachloride 645

RIGG, G. and J. L. CARPENTER. The Stormer Viscosimeter and the Value of Viscosity Determinations by its Use 901

RIPPETOE, J. R. A Note on the Determination of the Digestive Value of Papain 517

ROBINSON, C. S. and A. J. PATTEN. Neutral Ammonium Citrate Solution 443

ROGERS, ALLEN. Industrial Organic Chemistry. By S. P. Sadtler (Book Review) 628

ROGERS, W. F. The Inventor, the Public and the Law (Patent Symposium 320

ROST, C. O. and R. A. GORTNER. The Determination of Total Manganese in Soils 522

RUDNICK, P. Committee on Nitrogen, Fertilizer Division 225

RUDNICK, P. Fertilizer Chemistry—A Report of Progress 304

SABIN, A. H. The Manufacture of Varnishes and Kindred Industries, by J. G. McIntosh (Book Review) 472

SABIN, A. H. The Paint and Varnish Industry (A Note) 387

SADTLER, S. P. Chemicals, Oils and Paints by Tariff Board (Book Review 390

SADTLER, S. S. Methods of Organic Analysis, by H. C. Sherman Book Review 858

SAMMIS, J. L. A Simple Method for Purifying Drinking Water 681

SAVAGE, G. H. The Underwriters' Laboratories Extraction Apparatus. A Note 856

SCHAEFFER, J. A. The Colorimetric Determination of Iron in Lead and its Oxides 659

SCHAEFFER, J. A. The Determination of Lead Sulphate and the Ultimate Estimation of Sublimed White Lead in Rubber 836

SCHERUBEL, E. F. and W. D. RICHARDSON. A Modified Wiley Extraction Apparatus 220

SCHMIDT, A. H. Analyses of Some Fats of the American Buffalo (Bison) 592

SCHMIDT, W. A. Control of Dust in Portland Cement Manufacture by the Cottrell Precipitation Processes 719

SCHOLES, S. R. A Laboratory Glass-Furnace 683

SCHOLES, S. R. Arsenic in Glass 16

SCHOLES, S. R. and H. W. FOOTE. The Extraction of Potash and Alumina from Feldspar 377

SCHOLLENBERGER, C. J. Determination of Total Potassium in Minerals 436

SCHWARZ, R. A Rapid Microscopical Method for the Determination of Arsenic as Orpiment in Shellac 660

SHANNON, E. J. The Detection of Formic Acid in Fruit Products 526

SHARWOOD, W. J. A Note on Sampling 227

SHEPPARD, E. J. Pure Linseed Oil 14

SHERMAN, H. C. Allen's Commercial Organic Analysis, by Davis and Sadtler Book Review 550

SHERMAN, H. C. Food and Drugs, by Ernest J. Parry (Book Review) 858

SHERMAN, H. C. Pure Foods. Their Adulteration, Nutritive Value and Cost, by J. C. Olsen (Book Review) 234

SHERWIN, C. P. and C. E. MAY. Concerning the Sugar Content of Watermelons 585

SHRUVE, R. N. Suggested Modifications to the U. S. P. Assay of Opium 514

SILVERMANN, A. Glass Formulas. A Criticism 818

SINDALL, H. E. Commercial Cinnamon and Cassia 590

SKINNER, H. J. Committee on Standard Specifications and Methods of Analysis. Industrial Division Report 225

SKINNER, J. J. and J. H. BEATTIE. An Examination of City Street Sweepings 604

SLADE, W. C. A New Method for Testing Paint Films and Preservative Coatings for Iron and Steel 189

SMALLEY, F. N. Investigation of the Methods for the Determinations of Total Fatty Acids in Cotton Seed Foots. 893

SMITH, A. Some Chemical Problems of To-day, by R. K. Duncan (Book Review 233

SMITH, L. H. Altering the Composition of Indian Corn, by Seed Selection. 524

SMITH, O. C. A Self-Filling Measuring Wash Bottle 905

SMITH, T. O. An Automatic Pipette 47

SMITH, T. O. and B. E. CURRY. A Short Method for the Determination of Soluble Arsenic in Commercial Lead Arsenates 198

SMITH, W. B. The Index of Refraction of the Mixed Acids of Fatty Oils 36

SNELLING, W. O. Note on Protectors for Glass Stopcocks 613

SOSMAN, R. B. and A. L. DAY. The Expansion Coefficient of Graphite 490

SPEAR, E. B. and S. S. STRAHAN. The Determination of Zinc by Electroanalysis 889

SPENCE, D. and J. YOUNG. Comparison of some Methods for the Estimation of Sulfur in Vulcanized Rubber with Especial Reference to Electrolytic Oxidation 413

SPENCER, G. L. Alundum Crucibles in Gravimetric Analysis 614

STEWART, J. A Plan for the Support of Chemical Research and for the Better Teaching of Industrial Chemistry 616

STEWART, R. and C. T. HIRST. Comparative Value of Irrigated and Dry-farming Wheat for Flour Production 270

STONE, G. C. The Technical Analysis of Brass and the Non-ferrous Alloys, by Price and Meade (Book Review) 233

STRAHAN, S. S. and E. B. SPEAR. The Determination of Zinc, by Electroanalysis 889

STREET, J. P. Note on the Neutral Permanganate Method for the Availability of Organic Nitrogen 437

SUTERMEISTER, E. and H. R. RAFSKY. On the Quantitative Estimation of Sodium Hydroxide in Black Liquor 568

SWANSON, C. O. Acidity in Wheat Flour: Its Relation to Phosphorus and to Other Constituents 274

SWEETLAND, ERNST J. Recent Improvements in Filtration Methods. 114

SY, A. P. Apparatus for Fumeless Kjeldahl Nitrogen Digestion 680

TALBOT, H. P. Practical Chemistry for Engineering Students, by Arthur J. Hale (Book Review) 699

TANAKA, Y. On the Starch of Glutinous Rice and its Hydrolysis by Diastase 578

TANAKA, Y. On the Starch of Glutinous Rice and its Hydrolysis by Diastase. A Correction 918

TARTAR, H. V. and C. E. BRADLEY. A Comparative Study of Methods for the Determination of Hard and Total Soft Resins in the Hop. 209

TARTAR, H. V. and C. E. BRADLEY. The Ripening of Hops 591

TARTAR, H. V. and B. PILKINGTON. The Effect of Kiln-Drying at 145° F. on the Composition of the Hop 839

TAYLOR, E. R. The Manufacture of Carbon Bisulphide 557

TAYLOR, F. O. Report of Committee on Quantitative Methods 467

THIELE, L. A. The Manufacture of Gelatine 446

THOMAS, A. and G. F. WHITE. Studies on Fish Oils. III. Properties of Fish and Vegetable Oil Mixtures 878

THOMPSON, W. G. Occupational Poisoning in Chemical Trades 454

TILLOTSON, E. W. Jr. On the Density of some Borate and Silicate Glasses 820

TILLOTSON E. W. On the Surface Tension of Silicate and Borosilicate Glasses 651

TILLOTSON, E. W., JR. The Relation of the Refractive Index of Soda-Barium and Soda-Lime Glasses to their Chemical Composition 882

TILLOTSON, E. W., JR. The Relation of the Refractive Index of Soda-Lime Glasses to their Chemical Composition ... 246
TOCH, M. Paint Technology and Tests, by H. A. Gardner (Book Review) ... 389
TOCH, M. The Paint and Varnish Industry of the United States (Ed.) ... 241
TURRENTINE, J. W. A Note on the Determination of Iodides by Direct Titration ... 435
TURRENTINE, J. W. Composition of the Salines of the United States. I. Rock Salt, Artificial Brines and Mother Liquors from Artificial Brines ... 828
TURRENTINE, J. W. Composition of the Salines of the United States. II. Natural (Subterranean) Brines and Mother Liquors from Natural Brines ... 885
TURRENTINE, J. W. The Composition of the Pacific Kelps ... 431

UEHLING, E. A. The Carbon Dioxide Recorder as a Factor in Fuel Economy ... 123
UHLIG, E. C. Occupational Diseases (Ed.) ... 480

VAN HISE, C. R. Conservation (Ed.) ... 160

WAHL, R. Barleys Exhibited at the Second International Barley and Hop Prize Exhibit ... 230
WALKER, W. H. Corrosion of Iron and Steel, by J. N. Friend (Book Review) ... 549
WALKER, W. H. The Relative Corrosion of Iron and Steel Pipe as Found in Service ... 486
WALKER, W. H. and W. ARTHUR. Structure of Galvanized Iron ... 397
WALKER, W. H. and W. A. PATRICK. The Determination of Oxygen in Iron and Steel by Reduction in an Electric Vacuum Furnace ... 799
WALTERS, H. E. Determination of Manganese in Steel. A Note ... 387
WATKINS, W. H. The Fellow Who Doesn't Know Any Better (Ed.) ... 4
WEIDLEIN, E. R. Epinephrin from the Whale ... 636
WEIDLEIN, E. R. and H. W. EMERSON. Jamaica Camphor ... 33
WEITH, A. J. The Effect of "Lime Sulphur" Spray Manufacture on the Eyesight. A Note ... 917
WERTHEIMER, H. F. The German Patent System ... 464
WESSON, DAVID. The Chemist and the Cotton Seed Oil Industry in America (Address) ... 64
WEST, F. The Detection of Prussian Blue in Tea ... 528
WESTBY, G. C. Smelter Smoke Conservation ... 725
WHEELER, F. G. The Adaptation of the Centrifugal Pump to Chemical Problems ... 288
WHITAKER, M. C. A Dictionary of Applied Chemistry, Vol. I, by E. Thorpe (Book Review) ... 550
WHITAKER, M. C. Dictionary of Applied Chemistry, Vol. II, by E. Thorpe (Book Review) ... 698
WHITAKER, M. C. Industrial Chemistry, by Allen Rogers and A. B. Aubert (Book Review) ... 857
WHITAKER, M. C. Introduction (Perkin Medal Award) ... 131
WHITAKER, M. C. The Manufacture of Sulfuric Acid and Alkali, by G. Lunge (Book Review) ... 70
WHITE, G. F. A Study of the Viscosity of Fish Oils ... 106
WHITE, G. F. The Fluidity of Fish Oil Mixtures as an Additive Property ... 267
WHITE, G. F. and A. THOMAS. Studies on Fish Oils. III. Properties of Fish and Vegetable Oil Mixtures ... 878
WHITNEY, W. R. American Electrochemical Society Research Fund ... 546
WHITNEY, W. R. Carbon Brushes ... 242
WHITNEY, W. R. New Uses to Reduce Abuses in Conservation (Mineral Wastes Symposium) ... 182
WILEY, S. W. Unique Water Bath ... 454
WILKE, W. Combination of the Contact Process with the Ordinary Lead Chamber or Tower Systems; An Improvement in the Manufacture of Sulfuric Acid ... 840
WILLIAMS, F. M. New Forms of Apparatus for Gas Analysis ... 380
WILLIAMS, H. Paint and Varnish in the U. S. Navy. A Note ... 547
WILLIAMSON, C. S., JR. A Convenient Filtering Apparatus ... 222
WILLIAMSON, C. S., Jr. A Convenient Filtering Apparatus. Correction ... 310
WILLIAMSON, M. A. and P. A. BOECK. A New Type of Inorganic Filter for Laboratory Purposes ... 672
WILSNACK, G. C. and W. W. PATRICK. A New Volumetric Method for Tin ... 597
WISE, L. E. On the Indices of Refraction of China Wood Oil ... 497
WITHROW, J. R. Paper Pulps from Various Forest Woods, by H. E. Surface (Book Review) ... 918
WITHROW, J. R. The Effect of "Lime-Sulphur" Spray Manufacture on the Eyesight ... 735
WOOD, E. E. A Colorimetric Method for the Determination of Carbon in Iron and Steel. A Note of Protest ... 547
WOODMAN, A. G. The Determination of Benzaldehyde in Maraschino Cherries and Maraschino Liqueur. A Correction ... 856
WOODMAN, A. G. and L. DAVIS. The Determination of Benzaldehyde in Maraschino Cherries and Maraschino Liqueur ... 588
WORK, W. R. and J. M. KNOTE. A Modification of the Frary Electrodynamic Stirring Device ... 534

YERBY, W. J. Nigerian Tin Developments. (Consular Note) ... 624
YODER, P. A. Marking Porcelain and Silica Crucibles, etc. ... 567
YOUNG, J. and D. SPENCE. Comparison of some Methods for the Estimation of Sulfur in Vulcanized Rubber with Especial Reference to Electrolytic Oxidation ... 413

ZIMMERMANN, A. Laboratory Studies of Rennin ... 506
ZONS, F. W. and F. J. METZGER. A Volumetric Method for the Determination of Thorium in the Presence of Other Rare Earths. The Analysis of Monazite Sand ... 493

SUBJECT INDEX

THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY

VOL. IV, 1912

ACETIC Anhydride, Importations of. A Note..... 311
Acetylene, Commercial, The Determination of Phosphorus in. L. M. Dennis and W. J. O'Brien..... 834
Addresses..... 48, 125, —, 304, —, 454, 536, 614, 684, 749, —, 905
Agriculture and Food Chemistry, Division of Forty-fifth Meeting A. C. S. G. F. Mason, Sec..... 149
Alcohol, Absolute, A Still for. R. H. McKee..... 46
Alcohol, Ethyl, The Production of, from Waste Products. Editorial. A. Hirsch..... 478
Alcohol, The Denaturation of, with Pyridine. W. A. Hamor..... 850
Alcohol, The Distillation of. A. B. Adams..... 8
Alkali Industry in Great Britain during 1911, The. W. A. Hamor... 851
Alkaline Liquids, A New Filtering Material for. W. A. Hamor..... 385
Alkaloids, Micro-Chemical Tests for the Identification of Some of the. E. B. Putt..... 508
Alloy, A New, with Acid Resisting Properties. S. W. Parr..... 844
Alloys, Acid-Resisting. W. A. Hamor..... 852
Alloys, Aluminum. W. A. Hamor..... 916
Alloys, Increasing the Resistance of, to Chemical Action. W. A. Hamor..... 851
Alloys, Magnesium, The Casting of. W. A. Hamor..... 777
Alloys, Need of Special, for Special Purposes. Mineral Wastes Symposium. W. H. Bassett..... 167
Alloys, Recent Investigations on. W. A. Hamor..... 307
Alloys, Some New "Non-Corrosive." W. A. Hamor..... 463
Alumina, Silica and Potash from Feldspar. E. Hart..... 827
Aluminum Alloys. W. A. Hamor..... 916
Aluminum Foil, The Manufacture of. W. A. Hamor..... 463
Aluminum, Uses of. W. A. Hamor..... 620
Alundum Crucibles in Gravimetric Analysis. G. L. Spencer..... 614
Alundum not Constant in Weight. E. B. Forbes..... 544
American Chemical Society, Forty-fifth Annual Meeting. Program of Papers..... 147
American Chemical Society, Maine Section of the. H. Hanson..... 546
American Chemical Society, Organization of Rubber Section. D. A. Cutler..... 547
American Electrochemical Society Research Fund. W. R. Whitney.. 546
American Electrochemical Society, Twenty-first General Meeting, Boston, April 18th to 20th. Program..... 309
American Institute of Chemical Engineers, Fifth Annual Meeting, Detroit, Michigan..... 918
Ammonia Evaporation and Transformation in Soils. W. A. Hamor.. 777
Ammonia, Manufacture and Testing of Shipping Cylinders for Anhydrous. F. W. Frerichs..... 80
Ammonia, Synthetic. H. A. Bernthsen. Address..... 760
Ammonium Citrate Solution, Neutral. A. J. Patten and C. S. Robinson..... 443
Anaesthetics, The Chemistry of, IV: Chloroform. C. Baskerville and W. A. Hamor..... 212, 278, 362, 422, 499, 571
Analyst versus the Chemist, The. J. S. Brogdon. Address..... 684
Antimony Market, The State of the. W. A. Hamor..... 853
Apparatus, Laboratory, Two Pieces of. H. C. Chapin..... 453
"Argilite." W. A. Hamor..... 688
Arsenic, as Orpiment, in Shellac, A Rapid Microscopical Method for the Determination of. R. Schwarz..... 660
Arsenic, A Short Method for the Determination of Soluble, in Commercial Lead Arsenates. T. O. Smith and B. E. Curry..... 198
Arsenic in Glass. S. R. Scholes..... 16
Arsenic, The Wide Use of. W. A. Hamor..... 696

BABBITT Metal, Vanadium. W. A. Hamor..... 622
Bakelite Company, General, Starts Infringement Suits. A Note..... 548
Barleys Exhibited at the Second International Barley and Hop Prize Exhibit. R. Wahl..... 230
Beeswax, The Refractive Index of. L. Feldstein..... 498
Benzaldehyde in Maraschino Cherries and Maraschino Liqueur, The Determination of. A. G. Woodman and L. Davis..... 588
Benzaldehyde in Maraschino Cherries and Maraschino Liqueur, The Determination of. A Correction. A. G. Woodman..... 856
"Black Liquor," On the Quantitative Estimation of Sodium Hydroxide in. E. Sutermeister and H. R. Rafsky..... 568
Blast Lamp, A Substitute for the. W. A. Ernst..... 221
Bleaching Agent, "Persil" as a. W. A. Hamor..... 776
Bleaching of Linen, The. W. A. Hamor..... 621
Bleaching Powder as a Soap Substitute. W. A. Hamor..... 461
Boilers, The Use of Graphite in. W. A. Hamor..... 855
Book Reviews, 69, 155, 233, 313, 389, 471, 549, 626, 698, —, 857, 918
Addresses to Engineering Students, by various speakers. W. E. Hall..... 155
Allen's Commercial Organic Analysis, by Davis and Sadtler. H. C. Sherman..... 550
American Institute of Chemical Engineers, Transactions of the. Vol. III (1910). D. D. Berolzheimer..... 313
Analyse der seltenen Erden und der Erdsäuren, Die, by Meyer and Hauser. V. Lenher..... 858
Annual Tables of Constants and Numerical Data (Chemical, Physical and Technological), International Commission..... 70
Annual Tables of Constants and Numerical Data, Chemical, Physical and Technological, by International Commission of Seventh International Congress. L. E. Marrs..... 627
Assaying, A Manual of Fire, By C. H. Fulton. E. J. Hall..... 473
Brass and the Non-ferrous Alloys, The Technical Analysis of, by Price and Meade. Author's Note on Book Review. W. B. Price..... 469
Brass and the Non-ferrous Alloys, The Technical Analysis of, by Price and Meade. G. C. Stone..... 233
Breadmaking, The Chemistry of, by James Grant. C. A. Browne..... 550
Bread-making, The Technology of, etc., by W. Jago and W. C. Jago. C. A. Browne..... 313
Casein, Its Preparation and Technical Utilization, by Robert Scherer. O. Kress..... 391
Cellulose, Die Chemie der, with Particular Reference to the Textile and Cellulose Industries, by C. G. Schwalbe. H. S. Mork..... 472
Cellulose, Researches in, Vol. III, by Cross and Bevan. O. Kress 858
Cement Industry in 1911, The. Advance Chapter from U. S. Geological Survey Publication..... 698
Cement, Portland, by R. K. Meade. C. F. McKenna..... 698
Chemical Problems of To-day, Some, by R. K. Duncan. A. Smith..... 233
Chemicals, Oils and Paints, by Tariff Board. S. P. Sadtler..... 390
Chemiker Kalender, by Rudolf Biedermann. W. D. Richardson 472
Cocoa and Chocolate, Their Chemistry and Manufacture, by R. Whymper. C. A. Browne..... 473
Corrosion of Iron and Steel, by J. N. Friend. W. H. Walker..... 549
Dictionary of Applied Chemistry, A, by E. Thorpe, A Correction. Longmans, Green & Co..... 698
Dictionary of Applied Chemistry, A, Vol. I, by E. Thorpe. M. C. Whitaker..... 550
Dictionary of Applied Chemistry, A, Vol. II, by E. Thorpe. M. C. Whitaker..... 698
Fertilizer and Fertilizer Hints, by J. E. Halligan. F. B. Carpenter..... 472
Food and Drugs, by Ernest J. Parry. H. C. Sherman..... 858
Foods, Pure. Their Adulteration, Nutritive Value and Cost, by J. C. Olsen. H. C. Sherman..... 234
Fuel, Introduction to the Study of, by F. J. Brislee. E. G. Bailey..... 626
Gas, Circular on Regulations for Illuminating, by Bureau of Standards. W. F. Hillebrand..... 390
Handboek ten Dienste van de Suikerrietcultur en de Reitsuikerfabricage op Java, by H. C. P. Geerligs. C. A. Browne..... 69
Industrial Chemistry, by Allen Rogers and A. B. Aubert. M. C. Whitaker..... 857
Industrial Organic Chemistry, by S. P. Sadtler. Allen Rogers.. 628
Laboratory Apparatus Blue Book, The, by the Scientific Materials Co..... 550
Manures, The Manufacture of Chemical, by J. Fritsch. J. E. Breckenridge..... 233
Metallography of Iron and Steel, The, by Albert Sauveur. William Campbell..... 919

Metallurgical and Engineering Materials, Analysis of, by Henry Wysor. A. A. Blair ... 919
Metallurgie des Wolframs mit besonderer Berucksichtigung der Elektrometallurgie, Die, by Dr. Hans Mennicke. C. G. Fink ... 70
Metallurgy of Iron and Steel, by B. Stoughton. Wm. Brady ... 390
Oele, Die Chemie der trocknenden, by W. Fahrion. P. C. McIlhiney ... 313
Organic Analysis, Methods of, by H. C. Sherman. S. S. Sadtler ... 858
Paint Technology and Tests, by H. A. Gardner. M. Toch ... 389
Paper Pulps from Various Forest Woods, by H. E. Surface. J. R. Withrow ... 918
Plant Food. Its Sources, Conservation, Preparation and Application, by W. K. Bowker. F. B. Carpenter ... 234
Polarimetric der Erdöle, Die, by M. A. Rakusin. G. Mersereau 155
Practical Chemistry for Engineering Students, by Arthur J. Hale. H. P. Talbot ... 699
Radio Elements, The Chemistry of the, by F. Soddy. G. B. Pegram ... 627
Rubber, by P. Schidrowitz. W. C. Geer ... 389
Rubber Industry, The Chemistry of, by H. E. Potts. W. W. Evans ... 627
Snap Commercial Analysis, by F. W. Babington. W. F. Hillebrand ... 700
Strength of Materials, by Slocum and Hancock. W. Rautenstrauch ... 471
Sulfuric Acid and Alkali, The Manufacture of, by George Lunge. M. C. Whitaker ... 70
Technical Methods of Chemical Analysis, by George Lunge. F. J. Metzger ... 472
Technologie Papers of the Bureau of Standards, No. 3: Tests of the Absorptive and Permeable Properties of Portland Cement Mortars and Concretes, together with Tests of Dampproofing and Waterproofing Compounds and Materials, by Wig and Bates. W. A. Hamor ... 549
Varnishes, The Manufacture of, and Kindred Industries, by J. G. McIntosh. A. H. Sabin ... 472
Varnish-making, German, by Max Bottler. P. C. McIlhiney ... 628
Vinegars and Catsup, Interpretation of Standards, Analyses, etc., by R. O. Brooks. C. A. Browne ... 628
Boron, A New Use for. W. A. Hamor ... 622
Brand, The Abuse of. Mineral Wastes Symposium. A. D. Little ... 178
Bread, Salt-Rising, and Some Comparisons with Bread Made with Yeast. H. A. Kohman ... 20, 100
Bricks, Lava, The Occurrence of Efflorescence on. W. McGeorge ... 559
Briquetting Metallic Waste. W. A. Hamor ... 620
Bronze, Chrome-Nickel. W. A. Hamor ... 542
Bronze-Powder Industry, German. Trade Note ... 231
Bronze, The Influence of Additions to. W. A. Hamor ... 384
Brushes, Carbon. W. R. Whitney ... 242
Bureau of Mines. Appropriations. Note ... 69
Bureau of Mines, Natural gas Investigations of the. G. A. Burrell 614
Bureau of Mines, U. S., Description of the Explosion Test at the Experimental Mine of the, Feb. 24, 1912. G. S. Rice ... 488
Bureau of Standards Analyzed Samples. Note ... 388, 856

CALORIMETER Bomb, A New, Some Tests on. R. H. Jesse, Jr. ... 748
Calorimeter Bomb, A New, with Special Advantages as to Material of Construction and Method of Operation. S. W. Parr ... 746
Camphor, A Method for Assaying Spirits of. A. T. Collins ... 514
Camphor, Jamaica. H. W. Emerson and E. R. Weidlein ... 33
Carbon Bisulphide, The Manufacture of. E. R. Taylor ... 557
Carbon Dioxide Absorption Bottle. W. A. Koenig ... 844
Carbon Dioxide, A New Apparatus for the Determination of. E. W. Gaither ... 611
Carbon Dioxide, A New Apparatus for the Volumetric Determination of. H. W. Brubaker ... 599
Carbon Dioxide in Soils, On the Determination of. L. T. Bowser ... 265
Carbon Dioxide: Its Volumetric Determination. L. T. Bowser ... 203
Carbon Dioxide Recorder, The, as a Factor in Fuel Economy. E. A. Uehling ... 123
Carbon Disulphide, Italian Shipments of. W. A. Hamor ... 687
Carbonic Acid Cylinders, The Manufacture and Testing of. J. C. Minor, Jr. ... 88
Carbon in Iron and Steel, A Colorimetric Method for the Determination of. J. F. Kohout ... 378
Carbon in Iron and Steel, A Colorimetric Method for the Determination of. A Note. C. G. Hellman ... 548
Carbon in Iron and Steel, A Colorimetric Method for the Determination of. A Note of Protest. E. E. Wood ... 547
Carbon in Steel, The Determination of, by Direct Combustion in the Newest Form of Shimer Crucible, with the Aid of a Perforated Clay Disc. F. O. Kichline ... 683
Carbon Tetrachloride, The Chlorides of Carbon as Solvents, I. C. Baskerville and H. S. Riederer ... 645
Carbon Wastes. Mineral Wastes Symposium. J. A. Holmes ... 160
Cassia and Cinnamon, Commercial. H. E. Sindall ... 590
Cell, A Simple and Inexpensive Conductivity. C. A. Nowak ... 679
Cement Companies, Amalgamation of British. Consular Note ... 232
Cement, Free Lime in Portland. H. E. Kiefer ... 358
Cement Manufacture, Portland, Control of Dust in, by the Cottrell Precipitation Processes. W. A. Schmidt ... 719
Cement Manufacture, Portland, The Distribution of Power in. R. K. Meade ... 378
Cement, Natural *vs.* Portland. Geological Survey Note ... 388
Cement, Portland. W. A. Hamor ... 461
Cement Production and Trade of the Far East. Consular Note ... 694
Cement Production to 1910. Note ... 67
Cements and Plasters, Hardness of, and a Simple Chronographic Apparatus for Recording Set. C. F. McKenna ... 110
Cement, Setting Portland, Notes on a Study of the Temperature Gradients of. A. S. Cushman ... 728
Cerium, The Preparation and Properties of Metallic. A Correction. Alcan Hirsch ... 65
Charcoal, The Spontaneous Combustion of. W. A. Hamor ... 541
Cheese, Soy Bean. W. V. Linder ... 897
Chemical Industries in Sweden. Consular Report. T. H. Norton ... 51
Chemical Industries of France in 1911, The. W. A Hamor ... 849
Chemical Industries of Norway. Consular Report. T. H. Norton ... 691
Chemical Industry of Germany. Consular Note ... 695
Chemical Industry, The Latest Achievements and Problems of the. C. Duisberg. Address ... 749
Chemicals, Imports and Exports of. W. A. Hamor ... 852
Chemical Societies in New York City. Program of Meetings, 1912–1913 ... 918
Chlorine, The Cost of. W. A. Hamor ... 463
Chloroform from Bleaching Powder and Ethyl Alcohol, The Manufacture of. Address. F. W. Frerichs ... 345, 406
Chloroform, The Chemistry of Anaesthetics, IV. C. Baskerville and W. A. Hamor ... 212, 278, 362, 422, 499, 571
Chromium and Vanadium in Steel, The Determination of. D. J. Demorest ... 895
Chromium, The Determination of, and its Separation from Vanadium in Steels. J. R. Cain ... 17
Cinnamon and Cassia, Commercial. H. E. Sindall ... 590
Civil Service Examination. Announcement ... 69
Clay Products in 1910. Geological Survey Note ... 153
Coal, Deterioration and Spontaneous Heating of, in Storage. H. C. Porter and F. K. Ovitz ... 5
Coal Exports in 1910. Geological Survey Note ... 68
Coal Exports in 1911. Geological Survey Note ... 698
Coal Production, Illinois. Note ... 68
Coal Production, Nation's. Geological Survey Note ... 68
Coal Situation, Swedish. Consular Note ... 312
Coals, The Determination of Moisture in. E. H. Archibald and J. N. Lawrence ... 258
Coal, World's Production of. Note ... 67
Cobalt Driers. V. P. Krauss ... 731
Coke Making, Waste in. Geological Survey Note ... 697
Colors for Printing Inks and Similar Pigments, Some Practical Methods for Testing and Identifying. S. Levinson ... 661
Combustion, Surface. Editorial ... 77
Committee Reports ... 223, 467
Concrete, Cinder, Some Observations on the Disintegration of. G. Borrowman ... 405
Concrete, The Destructive Action of Acids on. W. A. Hamor ... 621
Concrete, The Production of Excessive Hydrogen Sulfid in Sewage Disposal Plants and Consequent Disintegration of the. W. M. Barr and R. E. Buchanan ... 564
Conservation. Editorial. C. R. Van Hise ... 160
Conservation, New Uses to Reduce Abuses in. Mineral Wastes Symposium. W. R. Whitney ... 182
Consular and Trade Notes ... 66, 154, 231, 312, 388, —, —, 624, 691, —, —, —
Copper, The Estimation of Oxygen and Occluded Gases in, and a Correction to the Electrolytic Assay in the Complete Analysis of. G. L. Heath ... 402
Copper, The Estimation of Oxygen and Occluded Gases in, etc. Author's Note. G. L. Heath ... 691
Copper Tools, "Tempered." W. A. Hamor ... 542
Cork Trade of the U. S. Consular Note ... 312
Corn, Indian, Altering the Composition of, by Seed Selection. L. H. Smith ... 524

Corrosion of Iron and Steel Pipe as Found in Service, The Relative. W. H. Walker 486
Corrosion of Iron and Steel, The. W. A. Hamor 619
Corrosion of Iron in Pure Water and Air Combined The Electrolytic Theory Again Confirmed. W. R. Fleming 480
Corrosion, The Prevention of Iron and Steel. W. A. Hamor 383
Cotton Mills, A Method for Determining the Value of Commercial Starches for Use in. G. M. MacNider 417
Cotton Seed Oil Industry in America, The Chemist and the. Address. David Wesson 64
Cottrell Precipitation Processes, Control of Dust in Portland Cement Manufacture by the. W. A. Schmidt 719
Cottrell Processes, The Electrical Precipitation of Suspended Particles by the. L. Bradley 908
Cream of Tartar, Pure, The Rapid Production of. W. A. Hamor 687
Cresol, The Bromine and Iodometric Methods for the Volumetric Determination of. C. M. Pence 518
Crucibles, Porcelain, Ordinary Writing Fluid for Marking. A Note. C. D. Mason 691
Crucibles, Porcelain, Silica, etc., Marking. P. A. Yoder 567
Crude Fiber, A Modification of the Sweeney Method for. C. Kennedy 600
Current Industrial News. W. A. Hamor 307, 382, 459, 539, 619, 686, 774, 849, 913
Customs Duties in Bolivia, Increased. Trade Note 154
Cyanogen and Hydrogen Cyanide, The Detection and Determination of. F. H. Rhodes 652
Cylinders, Manufacture and Testing of Shipping, for Anhydrous Ammonia. Address. F. W. Frerichs 80
Cylinders, The Manufacture and Testing of Carbonic Acid. J. C. Minor, Jr. 88

DEFLOCCULATION. E. G. Acheson 62
Diastafor in the Textile Industry. W. A. Hamor 385
Discussion, Carbon Wastes. Mineral Wastes Symposium 162
Discussion, Losses of Combined Nitrogen. Mineral Wastes Symposium 177
Discussion, Need of Special Alloys for Special Purposes. Mineral Wastes Symposium 169
Discussion, The Abuse of Brand. Mineral Wastes Symposium 179
Discussion, The Relation of the Silicate Industries to Conservation. Mineral Wastes Symposium 181
Discussion, Waste and Conservation of Potash and Phosphoric Acid. Mineral Wastes Symposium 171
Discussion, Zinc Losses. Mineral Wastes Symposium 165
Distilling Apparatus, An Improvement on the Kjeldahl. W. L. Hadlock 222
Driers, Cobalt. V. P. Krauss 731
"Duriron." W. A. Hamor 688
Dyes, Synthetic Organic, and Patents for the Manufacture of the Same, 1907–'11. W. A. Hamor 463
Dyestuffs, Modern, The Development of Hydrosulphites in their Relation to. P. S. Clarkson 733

EARTHENWARE Manufacture, Scientific Methods in. W. A. Hamor 383
Editorials 2, 76, 160, 240, 318, 396, 478, 556, 634, 706, 784, 864
Electrical Precipitation of Suspended Particles by the Cottrell Processes, The. L. Bradley 908
Electric Installations, A Dry Fire Extinguisher for. W. A. Hamor 386
Electro-Zincing, A New Process for. W. A. Hamor 621
Enamels for Sheet Steel. R. D. Landrum 561
Engine, A New Crude Oil. W. A. Hamor 689
Engines, Heavy Oil. W. A. Hamor 540
Epinephrin from the Whale. E. R. Weidlein 636
"Eponite," The Decolorization of Sugar Juice with. W. A. Hamor 383
Explosion Test, Description of the, at the Experimental Mine of the U. S. Bureau of Mines, Feb. 24, 1912. G. S. Rice 488
Extraction Apparatus, A Modified Wiley. W. D. Richardson and E. F. Scherubel 220
Extraction Apparatus, An Improved. W. C. Blasdale 302
Extraction Apparatus, The Underwriters' Laboratories. H. J. Cary-Curr 535
Extraction Apparatus, The Underwriters' Laboratories. A Note. G. H. Savage 856
Extraction Thimble, Notes on a New Form of. P. A. Boeck 303

FACTORY Inspection. W. A. Hamor 686
Factory Statistics, Swiss. Trade Note 697
Factory Ventilation. W. A. Hamor 686
Farmers' Materials, Imports and Exports of. Note 66
Fat, Butter, A Simple Test for the Determination of, in Butter. J. M. Doran 841
Fat in Desiccated Milk, A Modification of the Babcock Test as Applied to the Estimation of. N. G. Redmond 544
Fat in Sugared Evaporated Milk, Method for Determining. F. C. Broeman 672
Fats of the American Buffalo (Bison), Analyses of Some. A. H. Schmidt 592
Fatty Acids, Total, in Cotton Seed Foots, Investigation of the Methods for the Determinations of. F. N. Smalley 893
Fellow, The, Who Doesn't Know Any Better. Editorial. W. H. Watkins 4
Fermentation, Organisms, The Effect of Sulfurous Acid on. W. V. Cruess 581
Ferro-Tungsten, Electric Production of. Note 388
"Ferrozincing" or "Ironizing." W. A. Hamor 621
Fertilizer Chemistry, A Report of Progress. P. Rudnick 304
Fertilizer Chemists, Division of Forty-fifth Meeting A. C. S. J. E. Breckenridge, Sec 151
Fertilizer Division, Committee on Nitrogen. P. Rudnick, Chairman 225
Fertilizer Division, Committee on Phosphate Rock. A. M. Peter, Chairman 225
Fertilizer Division, Committee on Potash. J. E. Breckenridge, Chairman 224
Fertilizer Legislation, Committee on, Division Report. F. B. Carpenter, Chairman 223
Filter Feed, Automatic. T. A. Mitchell 613
Filtering Apparatus, A Convenient. C. S. Williamson, Jr. 222
Filtering Apparatus, A Convenient. Correction. C. S. Williamson, Jr. 310
Filtering Material, A New, for Alkaline Liquids. W. A. Hamor 385
Filter, Inorganic, for Laboratory Purposes, A New Type of. M. A. Williamson and P. A. Boeck 672
Filter Press, Factors Determining the Capacity of a. C. Almy, Jr., and W. K. Lewis 528
Filtration Methods, Recent Improvements in. E. J. Sweetland 114
Fire Bricks, The Melting Points of. W. A. Hamor 776
Fire Extinction. W. A. Hamor 309
Fire Extinguisher, A Dry, for Electric Installations. W. A. Hamor 386
Fluorspar, Valuation of. E. Bidtel 201
Fluorspar, Valuation of. A Correction. E. Bidtel 548
Food and Agricultural Chemistry, Division of Forty-fifth Annual Meeting A. C. S. G. F. Mason, Sec 149
Food and Drug Law, Pure, in Montana. A Note 69
Formaldehyde in Foods, Detection of. H. Leffmann 626
Formaldehyde-Phenol Condensation Products. L. H. Baekeland 737
Formic Acid in Fruit Products, The Detection of. F. L. Shannon 526
Fortoline. W. A. Hamor 462
Frary Electrodynamic Stirring Device, A Modification of the. J. M. Knote and W. R. Work 534
Freezing Mixtures, Non. W. A. Hamor 460
Frerichs, Dr. F. W. A Note 69
Fuel Economy in Factories. Address. C. E. Lucke 58
Fuel Economy, The Carbon Dioxide Recorder as a Factor in. E. A. Uehling 123
Fuels, Motor, The Properties of. W. A. Hamor 915
Fumes and Gases, Mineral Losses in. Mineral Wastes Symposium. F. G. Cottrell 182
Fungicides, Copper. W. A. Hamor 384
Furnace, An Electric Laboratory. R. C. Benner 43
Furnace, A New Type of Continuous. W. A. Hamor 916
Furnace Operation, The Need of Chemical Control in. R. C. Benner 691
Furnace, The Parkinson Patent. W. A. Hamor 854
Fusel Oil from Beet Molasses, The Composition of. J. L. Gooderham and M. C. Boswell 667
Fussy Administration. Editorial 634

GAS Analysis Apparatus, New Forms of. G. A. Burrell 297
Gas Analysis, New Forms of Apparatus for. F. M. Williams 380
Gas, Coal, The Continuous Purification of, with Weak Ammonia Liquor. J. G. O'Neill 876
Gas, Coke-Oven, The Use of. W. A. Hamor 542
Gases and Fumes, Mineral Losses in. Mineral Wastes Symposium. F. G. Cottrell 182
Gas Industry, The Present Status of, and its Outlook. C. E. Munroe 536
Gas Lighting, High Pressure. W. A. Hamor 915
Gas Liquor, Spent, The Pollution of Streams by. W. A. Hamor 776
Gas, Natural. Bureau of Mines Technical Paper. Note 388
Gas, Natural, Investigations of the Bureau of Mines. G. A. Burrell 614
Gas Production and Consumption in England. Trade Note 232
Gas, The Centenary of the Introduction of. Abstracts of Addresses 545
Gas, The Centenary of the Introduction of. Program 309
Gas, Utilization of Natural, in Hungary. Consular Note 312
Gas Works, English Municipal. Consular Note 312
Gauge, A New Vacuum. W. A. Hamor 622
Gelatine, The Manufacture of. L. A. Thiele 446
Geologist, Chief Geological Survey. Geological Survey Note 68

Gibbs, Wolcott. Address at the Unveiling of the Bust of C. E. Munroe. 48
Gibbs, Wolcott. Letter from C. L. Jackson 51
Glass, Arsenic in. S. R. Scholes 16
Glass, "Durobax." W. A. Hamor 852
Glasses, Borate and Silicate, On the Density of some. E. W. Tillotson, Jr 820
Glasses, Silicate and Borosilicate, on the Surface Tension of. E. W. Tillotson, Jr. 651
Glasses, Soda-Barium and Soda-Lime, The Relation of the Refractive Index of, to their Chemical Composition. E. W. Tillotson, Jr. 882
Glasses, Soda Lime, The Relation of the Refractive Index of, to their Chemical Composition. E. W. Tillotson, Jr 246
Glass Factories in Italy, The End of the Coöperative. J. B. Patch. 548
Glass Formulas A Criticism. A. Silverman 818
Glass Furnace, A Laboratory. S. R. Scholes 683
Glass Paving Blocks in France. Consular Note 154
Glass, Selenium. W. A. Hamor 539
Glass, "Triplex." W. A. Hamor 852
Gluten, Composition of Dry, and its Relation to the Protein Content of Flour. G. A. Olson 206
"Granacit." W. A. Hamor 621
Graphite in Boilers, The Use of. W. A. Hamor 855
Graphite, The Expansion Coefficient of. A. L. Day and R. B. Sosman 490
Guano Shipments to United States, Norwegian. Consular Note 154
Gum Tragacanth, The Volatile Acidity of, Compared with that of Indian Gum. W. O. Emery 374

HOP, A Comparative Study of Methods for the Determination of Hard and Total Soft Resins in the. H. V. Tartar and C. E. Bradley 209
Hop, The Effect of Kiln-Drying at 145° F. on the Composition of the. H. V. Tartar and B. Pilkington 839
Hops, The Ripening of. H. V. Tartar and C. E. Bradley 591
Humus, Soil, Studies on. S. Leavitt 601
Humus in Hawaiian Soil, The Determination of. W. P. Kelley and W. McGeorge 664
Hydrocarbons, The Synthesis of, at High Temperatures and Pressures. J. N. Pring and D. M. Fairlie 812
Hydrochloric Acid Gas, A Laboratory Generator for. E. Dowzard. 452
Hydrochloric Acid Gas, Laboratory Generator for. A Note. E. Hart 626
Hydrogen-Supply for Dirigible Balloons, A. W. A. Hamor 852
Hydrometers, The Graduation of. A Note. T. Kamoi 917
Hydrosulphites, The Development of, in their Relation to Modern Dyestuffs. P. S. Clarkson 733

INDUSTRIAL Chemistry, A Plan for the Support of Chemical Research and for the Better Teaching of. J. Stewart 616
Industrial Chemistry, Physical. Editorial. W. D. Bancroft 79
Industrial Chemistry, Progress in. R. Messel. Address 767
Industrial Chemists and Chemical Engineers, Division of Forty-fifth Meeting A. C. S. F. E. Gallagher, Sec 148
Industrial Diseases, Organization of Committees for Study of 547
Industrial Division, Committee on Standard Specifications and Methods of Analysis. Report. H. J. Skinner, Chairman 225
Industrial Division Report, Committee on Professional Code of Ethics. A. C. Langmuir, Chairman 226
Industrial Terms, Committee on Definition of, Industrial Division Report. C. Richardson, Chairman 226
Institute of Metals, The Autumn Meeting of the (British). W. A. Hamor 914
International Barley and Hop Prize Exhibit, Second, Barleys Exhibited at the. R. Wahl 230
International Congress Notes, Eighth 230
International Congress of Applied Chemistry. Announcement by Section I, Analytical Chemistry 548
International Congress of Applied Chemistry. Editorial 706
International Congress of Applied Chemistry, Eighth. Abstract of Announcement No. 3 310
International Congress of Applied Chemistry, Factory Visits and Excursions. Editorial 715
International Congress of Applied Chemistry. Our Guests. Editorial 634
International Congress of Applied Chemistry. Papers of Special Interest to Industrial Chemists and Chemical Engineers from the Proceedings of the Eighth. D. D. Berolzheimer 779
International Congress of Applied Chemistry, The Closing Session. Editorial 715
International Congress of Applied Chemistry, The Eighth. Editorial 556
International Congress of Applied Chemistry, The Inaugural Meeting at Washington. Editorial 707
International Congress of Applied Chemistry, The International Lectures. Editorial 712
International Congress of Applied Chemistry, The New York Meeting Editorial 711
International Congress of Applied Chemistry, The Sectional Addresses. Editorial 712
International Congress of Applied Chemistry, The Sectional Meetings. Editorial 713
International Congress of Applied Chemistry, The Social Features of the Congress. Editorial 713
International Congress of Applied Chemistry, The Societies at the Congress. Editorial 716
International Petroleum Commission in Vienna. Announcement 69
International Rubber Conference, Third. A Note 778
International Rubber Exhibition, The Third. W. A. Hamor 855
Inventions, Originality of. Anon 465
Inventor, The, the Public and the Law. Patent Symposium. W. F. Rogers 320
Iodides by Direct Titration, A Note on the Determination of. J. W. Turrentine 435
Iron and Steel, A Colorimetric Method for the Determination of Carbon in. J. F. Kohout 378
Iron and Steel, A New Method for Testing Paint Films and Preservative Coatings for. W. C. Slade 189
Iron and Steel Pipe, The Relative Corrosion of, as found in Service. W. H. Walker 486
Iron and Steel, The Determination of Oxygen in, by Reduction in an Electric Vacuum Furnace. W. H. Walker and W. A. Patrick 799
Iron, Corrosion of, in Pure Water and Air Combined, the Electrolytic Theory Again Confirmed. W. R. Fleming 480
Iron Furnace Blast, Oxygen Additions to. W. A. Hamor 622
Iron, Galvanized, Structure of. W. Arthur and W. H. Walker 397
Iron in Lead and its Oxides, The Colorimetric Determination of. J. A. Schaeffer 659
"Ironizing" or "Ferrozincing." W. A. Hamor 621
Iron Ore Production, Cuba. Note 68
Iron, Pig, the Commercial Sampling and Analysis of, Methods of the United States Steel Corporation for. The Chemists' Committee of the U. S. Steel Corporation 801
Iron Producing Region, Greatest in the World. Note 68

JOINT for Steel Pipe, A New. W. A. Hamor 623

KAMBARA Earth, The, A Decolorizing Material for Mineral Oils, Etc. K. Kobayashi 891
Kelp Industry, The Revival of the. W. A. Hamor 620
Kelp Proposition, The Business Aspect of the. F. P. Dewey 311
Kelps, Potash from the Pacific. Editorial. F. K. Cameron 76
Kelps, The Composition of the Pacific. J. W. Turrentine 431
Kupronizing. W. A. Hamor 463

LABORATORY and Plant 43, 110, 220, 288, 378, 446, 528, 609, 672, 744, 840, 898
Laboratory Support, A Simple Form of. T. L. Crossley 846
Lead and its Oxides, Iron in, The Colorimetric Determination of. J. A. Schaeffer 659
Lead Arsenates, A Short Method for the Determination of Soluble Arsenic in Commercial. B. E. Curry and T. O. Smith 198
Lead for Calking Joints. W. A. Hamor 688
Lead Furnace Fume, A Method for the Utilization of. L. S. Hughes 262
Lead Industry in 1910. Geological Survey Note 153
Lead, Red, A Study of the Variations of the Physical and Chemical Properties of. O. W. Brown and A. R. Nees 867
Lime, Free, in Portland Cement. H. E. Kiefer 358
"Lime-Sulphur" Spray Manufacture, the Effect of, on the Eyesight J. R. Withrow 735
"Lime-Sulphur" Spray Manufacture, the Effect of, on the Eyesight. A Note. A. J. Weith 917
Lithium, The Determination of. L. R. Milford 595
Lithographic Industry, Chemistry and the. B. P. Jaggard 470
Lithopone, The Manufacture of. W. A. Hamor 775
Litmus Paper, Laboratory Preparation of. E. W. Rice 229
Loeb, Morris. Editorial. L. H. Baekeland 784
Loeb, Morris. Obituary. C. Baskerville 846
Loeb, Morris. Resolutions Passed by the Various Chemical Societies on the Death of. Chemists' Club of New York City, American Chemical Society, Society of Chemical Industry 848
Lohmannizing. W. A. Hamor 384
Lubrication, Air Compressor. W. A. Hamor 774

MAGNESIUM Alloys, The Casting of. W. A. Hamor 777
Manganese in Steel, Determination of. J. J. Boyle 202
Manganese in Steel, Determination of. A Note. H. E. Walters 387
Manganese, The Bismuthate Method for. D. J. Demorest 19
Manganese, Total in Soils, The Determination of. R. A. Gortner and C. O. Rost 522

Market Report . 74, 158, 238, 316, 394, 476, 554, 632, 704, 782, 862, 922
Matsui, Dr. Naokichi. Obituary. Translation 230
Mayer, Frederick J. Obituary. J. V. V. Colwell 777
Meker Burner, The. W. D. Richardson 66
Melting Point Apparatus, A New. D. S. Pratt 47
Mercury Fulminate, Note on the Production of. C. E. Munroe 152
Metallizing Process, The Schoop. W. A. Hamor 853
Metallurgy. W. A. Hamor 916
Metals, New Composite Sheet. W. A. Hamor 622
Metals, Porous. W. A. Hamor 853
Metals, The Purity of Commercial. W. A. Hamor 462
Methane Apparatus, A Description of a Simple, and the Composition of Some Mine Gases. G. A. Burrell 96
Micro-chemical Tests for the Identification of Some of the Alkaloids. E. B. Putt 508
Milk, A Modification of the Babcock Test as Applied to the Estimation of Fat in Desiccated. N. G. Redmond 544
Milk and Cream, Desiccated, Notes on the Composition and Analysis of. R. S. Fleming 543
Milk, Sugared Evaporated, Method for Determining Fat in. F. C. Broeman 672
Milk, The Chlorine Content of. P. Poetschke 38
Mine Gases, The Composition of Some, and a Description of a Simple Methane Apparatus. G. A. Burrell 96
Mineral Losses in Gases and Fumes. Mineral Wastes Symposium. F. G. Cottrell 182
Mineral Production in North Carolina during 1908–'10, The 68
Mineral Wastes, Miscellaneous. Mineral Wastes Symposium. C. L. Parsons 185
Mineral Wastes Symposium 160
Mineral Wastes, The Chemists' Opportunity. C. L. Parsons 125
Miners' Diseases, Combating. Bureau of Mines Note 471
Mixer, A New Liquid. W. A. Hamor 460
Molybdenum, Some Applications of Wrought Tungsten and Molybdenum. W. D. Coolidge. Editorial 2
Monazite Sand, The Analysis of. A Volumetric Method for the Determination of Thorium in the Presence of other Rare Earths. F. J. Metzger and F. W. Zons 493
Monel Metal. R. H. Gaines 354

NAPHTHALENE, Extraction with. W. A. Hamor 308
Neon Tubes, Lighting by. W. A. Hamor 620
New Publications. D. D. Berolzheimer 70, 156, 234, 314, 391, 474, 551, 628, 700, 779, 859, 920
Nitrates, The Manufacture of, from the Atmosphere. W. A. Hamor . . 619
Nitric Acid Industry, "Vitreosil" in the. W. A. Hamor 913
Nitrification, The Influence of Carbon upon. H. W. Clark and G. O. Adams 272
Nitrogen Apparatus for Fumeless Kjeldahl Digestion. A. P. Sy 680
Nitrogen, Atmospheric, A Process for the Fixation of. W. A. Hamor 619
Nitrogen, Committee on. Division Report. P. Rudnick, Chairman . . 225
Nitrogen Fixation, The Serpek Process of. W. A. Hamor 385
Nitrogen, Losses of Combined. Mineral Wastes Symposium. J. D. Pennock 172
Nitrogen, Organic, Activity of, as Measured by the Alkaline Permanganate Method. C. H. Jones 438
Nitrogen, Organic, Note on the Neutral Permanganate Method for the Availability of. J. P. Street 437
Nitrogeneous Materials, Low Grade, The Effect of the "Wet Process" on the Availability of. B. L. Hartwell and F. R. Pember 441
Nitrogen, Oxidation of Atmospheric, and Development of Resulting Industries in Norway. S. Eyde. Address 771
Nomenclature, American Commission on Organic. M. T. Bogert . . . 309
Notes and Correspondence 65, 152, 227, 309, 386, 464, 543, 623, 690, 777, 855, 917
Nozzles, Spray, A New Pattern in. W. A. Hamor 386

OBITUARIES 230, 777, 846, 917
Occupational Diseases. Editorial. E. C. Uhlig 480
Oil, China Wood, A Method of Examining. P. C. McIlhiney 496
Oil, China Wood, On the Indices of Refraction of. L. E. Wise 497
Oil Engine, A New Crude. W. A. Hamor 689
Oil from Sunflower Seed. Consular Note 232
Oil in Alaska. Geological Survey Note 69
Oil in Grains, A Rapid Control Method for the Determination of. E. P. Harding and L. L. Nye 895
Oil Mixtures, Fish, The Fluidity of, as an Additive Property. G. F. White 267
Oil of Pochote, The. S. Lomanitz 625
Oil, Palm, Industry of West Africa. Consular Note 154
Oil, Perilla. C. P. Fox 229
Oil, Pure Linseed. E. J. Sheppard 14
Oils, Apparatus for the Examination and Study of the Behavior of Valve and Cylinder and other Petroleum Lubricating, in Saturated and Superheated Steam, Carbon Dioxide, Air and other Gases. P. H. Conradson 744
Oils, Essential, The Determination of Eucalyptol (Cineol) in. F. D. Dodge 592
Oils, Fatty, The Index of Refraction of the Mixed Acids of. W. B. Smith 36
Oils, Fish, A Study of the Viscosity of. G. F. White 106
Oils, Fish, Studies on. III. Properties of Fish and Vegetable Oil Mixtures. G. F. White and A. Thomas 878
Oil, Shark's Liver, Industry Proposed. Consular Note 312
Oils, Mineral, etc., A Decolorizing Material for. The Kambara Earth. K. Kobayashi 891
Oil, Solid, as a Marine Fuel. W. A. Hamor 915
Oils, Petroleum Illuminating and Lubricating, Apparatus and Method for Sulphur Determination in. P. H. Conradson 842
Oils, Petroleum Lubricating, Apparatus and Method for "Carbon Test" and Ash Residue in. P. H. Conradson 903
Oils, Wood Preserving, The Value of the Higher Phenols in. S. Cabot 206
Opium, Some Data on the Manufacture of Smoking, and its Chemical Composition. A. B. Adams and J. M. Doran 429
Opium, Suggested Modifications to the U. S. P. Assay of. R. N. Shreve 514
Organic Nomenclature, American Commission on. A Note 309
Original Papers, 5, 80, 189, 242, 338, 397, 480, 557, 636, 719, 789, 867
Orsat Apparatus, A New Form of. L. M. Dennis 898
Oxygen in Iron and Steel, The Determination of, by Reduction in an Electric Vacuum Furnace. W. H. Walker and W. A. Patrick 799
Oxygen, The Consumption of. W. A. Hamor 915
Oxygraph, The. W. A. Hamor 775
Ozone, The Industrial Uses of. W. A. Hamor 459
Ozone, The Purification of Air by. W. A. Hamor 542
Ozonized Air, Accelerating Paint Drying with. W. A. Hamor 687

PACKING in Steam Plants. W. A. Hamor 461
Paint and Varnish in the U. S. Navy. A Note. H. Williams 547
Paint Drying, Accelerating, with Ozonized Air. W. A. Hamor 687
Paint and Varnish Industry of the United States, The. Editorial. M. Toch 241
Paint and Varnish Industry, The. A. H. Sabin 387
Paint Films and Preservative Coatings for Iron and Steel, A New Method for Testing. W. C. Slade 189
Paint Production in 1911. Geological Survey Note 697
Paints. The Stormer Viscosimeter and the Value of Viscosity Determinations by its Use. G. Rigg and J. L. Carpenter 901
Papain, A Note on the Determination of the Digestive Value of. J. R. Rippetoe 517
Papermaking, Problems in. W. A. Hamor 914
Papermaking, Progress of the Chemistry of. W. A. Hamor 307
Patent Rights, An Experiment in Public Administration of. The Research Corporation. Editorial. F. G. Cottrell 864
Patents and Chemical Industry in the United States. Patent Symposium. B. Herstein 328
Patent Litigation, American, The Incongruities of. Editorial. L. H. Baekeland 785
Patents, English 701
Rubber, Attaching, to Metals. Royston 701
Silicates, Alkali, in Powder form. Justice 701
Patents, United States . . . . . 72, 157, 236, 315, 393, 475, 552, 629, 702, —, 860, 921
Alumina and Potash from Feldspar, Process for Extracting. Peacock 860
Aluminium Nitride, Process of Manufacturing. Serpek 703
Ammonium Carbonate, Method of Making. Bueb 237
Carbon-black, Method of Producing. Snee 860
Carbon, Method of Treating. Smith 702
Chlorids of Carbon, Apparatus for Producing. MacKaye 393
Concentration of Mineral Substances, Art of. Hyde 552
Copper, Process of Refining. Rockey and Eldridge 921
Crystals, Method of Producing. Dow 72
Electrolytic Apparatus. Seward and Kugelgen 315
Electrolytic Deposit of Metals, Process for the. Rodeck 236
Fats, Oils and Fish-oils, Process for Converting, into Like Bodies of Higher Melting Point. Wilbuschewitsch 630
Fatty Materials, Hydrogenating. C. Ellis 702
Ferric Oxide, Manufacture of. Gill 315
Fullers' Earth and Analogous Materials, Method of Separating and Purifying. Ruprecht 629
Furnace, Electric. Arsem 393
Furnace, Induction. Fleming 552
Gas, Process of Treating Natural. Knapp 553
Hides, Process of Curing. James 629

Hydrogen, Apparatus for the Separation of, from a Gaseous Mixture. Carl von Linde..... 630
Hydrogen, Process for the Production of, from Gas Mixtures Containing Hydrogen. von Linde..... 475
Hydrogen, Process of Purifying. Rabenalt..... 860
Iron Ore, Method of Reducing. Grondal..... 861
Isoprene, Manufacture of. Silberrad..... 553
Lead and Lead Alloys, Process of Refining. Wemple..... 72
Lead Compounds, Production of. Hughes..... 703
Metals and Alloys, Refined, Method of Producing. Green..... 860
Metals, Apparatus for Melting and Mixing, in Vacuums. Simpson..... 475
Metals from their Ores, Process and Apparatus for Recovering. Potter..... 631
Metals, Process of and Apparatus for Making Clad. Monnot..... 72
Metals, Treatment on. Kelly..... 475
Mineral Substances, Art of Concentration of. Hyde..... 552
Nitrates, Alkaline and Earthy-Alkaline, Process of Manufacture of. Guye, Darier and von Vloten..... 860
Nitrates and Nitric Acid, Process of Making. Schönherr and Brode..... 921
Nitric Acid, Process of Concentrating. Sohlman and Lundholm 393
Nitrogen Compounds, Method of Producing. Acker..... 552
Nitrogen Compounds, Method of Producing, from Carbids. Frank..... 73
Nitrogenous Compounds, Preparing. Summers..... 861
Nitrogen, Process for Conversion of Lower Oxids of, to Higher Oxids of Nitrogen. Sparee..... 315
Nitrogen, Process of Binding and Utilizing Atmospheric. Sinding-Larsen..... 702
Nitrogen, Substantially Pure, from the Air, Process of Obtaining. Blagburn..... 861
Nitrous Gases, Process of Absorbing. Pauling..... 921
Oils, Caoutchouc, Resins and the Like, Process of Manufacturing Substitutes for. Lilienfeld..... 861
Petroleum, Treatment of. Dubbs..... 157
Petroleum, Utilizing Acid Sludge from Refining. Black and Chappell..... 703
Phenol Resins, Process of Forming Fusible. Alysworth..... 631
Phosphates, Process of Making Superphosphates. Williams..... 157
Potash and Alumina from Feldspar, Process for Extracting. Peacock..... 860
Rare Gases, Method of Extracting, from the Air. Claude..... 631
Refractory Article and Method of Making it. Hall..... 703
Resin from Waste Products, Methods of Recovering. Huggins.. 553
Rubber Waste, Process for Reclaiming Vulcanized. Heller..... 630
Salt-Making. Frasch..... 237
Sewage and Water, Process of Purifying. Darnall..... 237
Sludge, Utilizing Acid, from Refining Petroleum. Black and Chappell..... 703
Sodium Cyanide, The Manufacture of. Acker..... 552
Steel, Manufacture of. Mackie..... 631
Still, A Self-cleaning. McCune..... 73
Tin Chlorid, Method of Making Anhydrous. Baillio..... 552
Water and Sewage, Process of Purifying. Darnall..... 237
Welding Metals, Process of. Mucas..... 475
White Lead, Continuous Process of Making, and Apparatus Therefor. Ellis..... 157
Patent Symposium..... 320
Patent System, Report of the Delegate to the Joint Conference on the. C. E. Munroe..... 466
Patent System, The Abuses of Our. Patent Symposium. L. H. Baekeland..... 333
Patent System, The German. H. F. Wertheimer..... 464
Patent System, The U. S. Editorial. W. M. Grosvenor..... 318
Peat Fuel for the Production of Power. W. A. Hamor..... 853
Peat, The Utilization of. W. A. Hamor..... 689
Perkin Medal Award..... 131
Perkin Medal Award, Address of Acceptance. Herman Frasch..... 134
Perkin Medal Award. Geology of the Sulphur and Sulphur Oil Deposits of the Coastal Plain. Address. Capt. A. F. Lucas..... 140
Perkin Medal Award, Introduction. M. C. Whitaker..... 131
Perkin Medal Award, Presentation Address. C. F. Chandler..... 132
Perkin Medal Award. Sulphur Mines of the Union Sulphur Company in Louisiana. Illustrated Lecture. F. H. Pough..... 143
Permanganate Method, Alkaline, Activity of Organic Nitrogen as Measured by the. C. H. Jones..... 438
Permanganate Method, Neutral, for the Availability of Organic Nitrogen, Note on the. J. P. Street..... 437
Permutite, The Purification and Softening of Water by. W. A. Hamor. Editorial..... 240
"Persil" as a Bleaching Agent. W. A. Hamor..... 776
Petroleum Commission, The International. Note..... 69
Petroleum Output of the World. Trade Note..... 232
Pharmaceutical Chemistry, Division of, Forty-fifth Meeting A. C. S. F. R. Eldred, Sec..... 150
Pharmaceutical Chemistry, The Scope of. Editorial. F. R. Eldred.. 396
Pharmacopoeia, U. S., Progress of the Work on the Revision of the. J. P. Remington..... 457
Phenol-Formaldehyde Condensation Products. L. H. Baekeland..... 737
Phenol-Formaldehyde Condensation Products, A Correction. L. H. Baekeland..... 857
Phenol, Rapid and Accurate Methods for Determining. L. V. Redman and E. O. Rhodes..... 655
Phenols, The Phenomenon of the Apparent Disappearance of the Higher Boiling, in Creosoted Wood and its Explanation. S. Cabot..... 266
Phenols, The Value of the Higher, in Wood-Preserving Oils. S. Cabot..... 206
Phosphate Manufacture, A Method for Testing out Problems in Acid. F. B. Porter..... 264
Phosphate Rock, Committee on. Division Report. A. M. Peter, Chairman..... 225
Phosphate Rock, The Accurate Volumetric Determination of Phosphoric Acid in. J. G. Fairchild..... 520
Phosphates, Soil, The Effect of Ignition on the Solubility of. C. B. Lipman..... 663
Phosphoric Acid and Potash, Waste and Conservation of. Mineral Wastes Symposium. F. K. Cameron..... 169
Phosphorus in Commercial Acetylene, The Determination of. L. M. Dennis and W. J. O'Brien..... 834
Phosphorus, Inorganic, in Plant Substances, A Method of Estimation. R. C. Collison..... 606
Phosphorus Slag as an Insecticide. W. A. Hamor..... 621
Pipe, Reinforced Galvanized Spiral. W. A. Hamor..... 854
Pipes, The Location of Underground. W. A. Hamor..... 777
Pipette, An Automatic. T. O. Smith..... 47
Plasters and Céments, Hardness of, and a Simple Chronographic Apparatus for Recording Set. C. F. McKenna..... 110
Platinum Group, Volatility of Metals of the. Note..... 470
Platinum in Ores and Bullion, The Direct Determination of Small Amounts of. F. P. Dewey..... 257
Platinum Market, The State of the..... 850
Platinum Production, Good Increase in. Geological Survey Note... 697
Plumbism in New York City. W. A. Hamor..... 849
"Plumboxan." W. A. Hamor..... 916
Poisoning, Mercury. W. A. Hamor..... 686
Poisoning, Occupational, in Chemical Trades. W. G. Thompson,... 454
Potash and Alumina from Feldspar, The Extraction of. H. W. Foote and S. R. Scholes..... 377
Potash and Phosphoric Acid, Waste and Conservation of. Mineral Wastes Symposium. F. K. Cameron..... 169
Potash and Salt Statistics, German. Consular Note..... 696
Potash, Committee on. Division Report. J. E. Breckenridge, Chairman..... 224
Potash from the Pacific Kelps. Editorial. F. K. Cameron..... 76
Potash Interests, German. Consular Note..... 154
Potash, Relation of Active, to Pot Experiments. G. S. Fraps..... 525
Potash, Seaweed and Iodine. F. K. Cameron..... 690
Potash, Seaweed and Iodine. A Criticism. H. Knudsen..... 623
Potash, Silica and Alumina from Feldspar. E. Hart..... 827
Potash, The Production of Available, from the Natural Silicates. A. S. Cushman and G. W. Coggeshall..... 821
Potassium Content of Minerals, The Utilization of the. W. A. Hamor 384
Potassium in Minerals, Determination of Total. C. J. Schollenberger.. 436
Power, The Distribution of, in Portland Cement Manufacture. R. K. Meade..... 378
Price, Thomas, Obituary. A. F. Price..... 917
Professional Code of Ethics, Committee on, Industrial Division. A. C. Langmuir, Chairman..... 226
Protein Content of Flour, Composition of Dry Gluten and its Relation to the. G. A. Olson..... 206
Prussian Blue in Tea, The Detection of. F. West..... 528
Pump, A Double-oiling System. W. A. Hamor..... 689
Pump, Air, A New Automatic Water-jet. W. A. Hamor..... 854
Pump, Air, A New Water-Jet. W. A. Hamor..... 854
Pump, Centrifugal, The Adaptation of the, to Chemical Problems. F. G. Wheeler..... 288
Pumps. W. A. Hamor..... 385

QUANTITATIVE Methods, Report of Committee on. F. O. Taylor 467

RATISAL. A Trap Substitute. W. A. Hamor 486
Recent Inventions. C. L. Parker
72 187 236 318 393 478, 552, 629 701, 860, 921
Recent Journal Articles. Classified List. D. D. Berolzheimer
54 136 235 314 392 474 551 629 704, 781 859 920
Refractories, Specifications for. W. A. Hamor 686
Refrigerating Agent, Methyl Chloride as a. W. A. Hamor 687
Rennin, Laboratory Studies of. A. Zimmermann 806
Research and Analytical Chemistry. A Plan for Organized, in Successful Chemical Manufacturing. W. C. Ferguson 905
Research, Chemical. A Plan for the Support of, and for the Better Teaching of Industrial Chemistry. J. Stewart 616
Research Corporation, The. An Experiment in Public Administration of Patent Rights. Editorial. F. G. Cottrell 864
Research Fund, American Electrochemical Society. W. R. Whitney 546
Research Scholarship, The Andrew Carnegie. Announcement 917
Resenes of Resins and Oleoresins, The. C. H. Herty and W. S. Dickson 495
Resins, Hard and Total Soft, in the Hop, A Comparative Study of Methods for the Determination of. C. E. Bradley and H. V. Tartar 209
Rivers, What our, Carry. Geological Survey Note 67
Rubber, Apocynum or Indian Hemp. C. P. Fox 387
Rubber, Artificial, from Seaweed. W. A. Hamor 542
Rubber, Comparison of some Methods for the Estimation of Sulfur in Vulcanized, with Especial Reference to Electrolytic Oxidation. D. Spence and J. Young 413
Rubber Contents in Raw and Vulcanized Rubber, Testing Methods of. W. A. Ducca 372
Rubber, Exhibition, The Third International. W. A. Hamor 855
Rubber Section, Meeting of the Forty-fifth Meeting A. C. S. F. J. Maywald, Sec. 152
Rubber, Sublimed White Lead in, The Determination of Lead Sulphate and the Ultimate Estimation of. J. A. Schaeffer 836
Rubber Substitute, Another. W. A. Hamor 850
Rubber Test Pieces, Straight, A Punch for. H. P. Mills 452

SALINES of the U. S., Composition of the. I. Rock Salt, Artificial Brines and Mother-liquors from Artificial Brines. J. W. Turrentine 828
Salines of the U. S., Composition of the. II. Natural (Subterranean Brines and Mother Liquors from Natural Brines. J. W. Turrentine 885
Saltpeter Industry, The Condition of the Chilean. W. A. Hamor 687
Samples, Analyzed, Bureau of Standards. Note. 388, 856
Samples, Laboratory, Contamination of, by Iron Derived from Crushing Machinery. V. Lenher 471
Sampling, A Note on. W. J. Sharwood 227
Sampling Cone. C. W. Kneff 682
Saratoga Mineral Waters, Recent Analyses of the. L. R. Milford 593
Scientific Societies 147
Sewage Disposal Plants, The Production of Excessive Hydrogen Sulfid in, and Consequent Disintegration of the Concrete. W. M. Barr and R. E. Buchanan 564
Sewage, Tannery Wastes in. W. A. Hamor 382
Shellac, A Rapid Microscopical Method for the Determination of Arsenic, as Orpiment, in. R. Schwarz 660
Silicate Industries, The Relation of the, to Conservation. Mineral Wastes Symposium. A. V. Bleininger 180
Silk, Artificial, Industry, The Status of the. W. A. Hamor 850
Silks, Artificial. W. A. Hamor 916
Siloxide. W. A. Hamor 308
Smelter Smoke Conservation. G. C. Westby 725
Smoke Problem, Lectures on the. Announcement. R. C. Benner 626
Soaps, The Classification of. W. A. Hamor 541
Soap Substitute, Bleaching Powder as a. W. A. Hamor 461
Soil Phosphates, The Effect of Ignition on the Solubility of. C. B. Lipman 663
Soils, On the Determination of Carbon Dioxide in. L. T. Bowser 265
Soils, The Determination of Total Manganese in. R. A. Gortner and C. O. Rost 522
Solvents, The Chlorides of Carbon as. I. Carbon Tetrachloride. C. Baskerville and H. S. Riederer 645
Soy Bean Cheese. W. V. Linder 897
Standard Specifications and Methods of Analysis, Committee on. Industrial Division Report. H. J. Skinner, Chairman 225
Starches, A Method for Determining the Value of Commercial, for Use in Cotton Mills. G. M. MacNider 417
Starch, On the, of Glutinous Rice and its Hydrolysis by Diastase. Y. Tanaka 578
Starch, On the, of Glutinous Rice and its Hydrolysis by Diastase. A Correction. Y. Tanaka 918
Steam Consumption, The Measurement of. W. A. Hamor 623
Steam Generation, Developments in. W. A. Hamor 462
Stearic Acid, A New Process for Producing. W. A. Hamor 687
Steel and Iron, A Colorimetric Method for the Determination of Carbon in. I. E. Kolbout 378
Steel and Iron, A New Method for Testing Paint Films and Preservative Coatings for. W. C. Slade 189
Steel and Iron Pipe, The Relative Corrosion of, as Found in Service. W. H. Walker 486
Steel and Iron, The Determination of Oxygen in, by Reduction in an Electric Vacuum Furnace. W. H. Walker and W. A. Patrick 799
Steel, Chromium and Vanadium in, The Determination of. D. J. Demorest 895
Steel Corporation, The Methods of the U. S., for the Commercial Sampling and Analysis of Pig Iron. The Chemists' Committee of the U. S. Steel Corporation 801
Steel, Determination of Manganese in. J. J. Boyle 202
Steel, Determination of Manganese in. A Note. H. E. Walters 387
Steels, The Determination of Chromium and its Separation from Vanadium in. J. R. Cain 17
Steel, The Determination of Carbon in, by Direct Combustion in the Newest Form of Shimer Crucible with the Aid of a Perforated Clay Disc. F. O. Kichline 683
Steel, Titanium and Alloys of 697
Still, An Electric, Adapted for Difficult Distillations. I. C. Allen and W. A. Jacobs 118
Stirring Device, A Modification of the Frary Electrodynamic. J. M. Knote and W. R. Work 534
Stopcocks, Note on Protectors for Glass. W. O. Snelling 613
Storage Battery Sludge, The Utilization of. W. A. Hamor 462
Street Sweepings, City, An Examination of. J. J. Skinner and J. H. Beattie 604
Suction Hose, The Manufacture of. W. A. Hamor 688
Sugar Content of Watermelons, Concerning the. C. P. Sherwin and C. E. May 585
Sugar Juice, The Decolorization of, with "Eponite." W. A. Hamor 383
Sugar, Temperature Corrections in Raw, Polarizations. W. D. Horne 41
Sulfite Industry, Development of the. W. A. Hamor 913
Sulfite Liquor, The Utilization of. W. A. Hamor 687
Sulfur and Sulfur Oil Deposits of the Coastal Plain, Geology of the. Perkin Medal Award Address. Capt. A. F. Lucas 140
Sulfur Determination in Petroleum Illuminating and Lubricating Oils, Apparatus and Method for. P. H. Conradson 842
Sulfur Dioxide from Iron Pyrites. W. A. Hamor 852
Sulfuric Acid, An Improvement in the Manufacture of. Combination of the Contact Process with the Ordinary Lead Chamber or Tower System. W. Wilke 840
Sulfuric Acid, Aromatic, An Improved Method of Assay for. L. A. Brown 512
Sulfuric Acid Chambers, Improved. T. H. Norton 532
Sulfuric Acid, Contact, from Brimstone. G. W. Patterson and L. B. Cheney 723
Sulfuric Acid Manufacture, The Contact Process of. W. A. Hamor 462
Sulfuric Acid Stock, Calculation of, by Approximate *vs.* Accurate Methods. A Special Slide Rule. H. C. Moore 677
Sulfur, in Roasted Blende, A Rapid Determination of. C. C. Nitchie 30
Sulfur in Vulcanized Rubber, Comparison of some Methods for the Estimation of, with Especial Reference to Electrolytic Oxidation. D. Spence and J. Young 413
Sulfur Mines in Mexico. Consular Note 232
Sulfur Mines of the Union Sulfur Company in Louisiana. Perkin Medal Award Address. F. H. Pough 143
Sulfurous Acid, The Effect of, on Fermentation Organisms. W. V. Cruess 581
Sulfur, Pyrite and Sulfuric Acid. Geological Survey Note 695

TANNERY Wastes in Sewage. W. A. Hamor 382
Tea, The Detection of Prussian Blue in. F. West 528
Temperature, The Control of, in the Operations of Analytical Chemistry. Address. T. W. Richards 910
Textile Industry, Diastafor in the. W. A. Hamor 385
Textilose. W. A. Hamor 621
Thoria, Extraction of. C. Baskerville 821
Thorium, A Volumetric Method for the Determination of, in the Presence of Other Rare Earths. The Analysis of Monazite Sand. F. J. Metzger and F. W. Zons 493
Tin, A New Volumetric Method for. W. W. Patrick and G. C. Wilsnack 597
Tin Developments, Nigerian. Consular Note. W. J. Yerby 624
Tin Exports, Malaysian. Consular Note 312
Titanium and Alloys of Steel. Geological Survey Note 697
Trap Substitute, A, "Ratisal." W. A. Hamor 386
Tungsten Production in the United States in 1911. Geological Survey Note 153

Tungsten, Some Applications of Wrought Tungsten and Molybdenum Editorial. W. D. Coolidge ... 2

UNIVERSITY of Washington, Design and Equipment of the Chemical Engineering Laboratory at the. H. K. Benson ... 609

VACUUM Evaporator Tubes, Heat Transmission in. W. A. Hamor 689
Valve for Gas Cylinders, A New Form of. W. A. Hamor ... 622
Valve, Modified Bunsen. L. R. Milford ... 845
Valve, New Tank. W. A. Hamor ... 386
Vanadium and Chromium in Steel, The Determination of. D. J. Demorest ... 895
Vanadium, A New Method for the Determination of; An Explanation. J. R. Cain and D. J. Demorest ... 256
Vanadium, A New Method for the Determination of. D. J. Demorest 249
Vanadium in Steels, Ores, Etc., A Rapid Method for the Determination of, Based on its Quantitative Inclusion by the Phosphomolybdate Precipitate. J. R. Cain and J. C. Hostetter ... 250
Vanadium in Steel, The Rapid Determination of. F. Garratt 256
Vanadium, The Determination of Chromium and its Separation from Vanadium in Steels. J. R. Cain ... 17
"Vanalium." W. A. Hamor ... 688
Vanillin, A New Colorimetric Method for the Determination of, in Flavoring Extracts. O. Folin and W. Denis ... 670
Vanillin, Difficulties in the Colorimetric Estimation of. W. S. Hubbard ... 669
Ventilator, Air-Jet Chimney. W. A. Hamor ... 689
Victor Meyer Apparatus, A Modified. H. C. Chapin ... 684
Viscosimeter, The Stormer, and the Value of Viscosity Determinations by its Use. G. Rigg and J. L. Carpenter ... 901
Volatile Matter Determinations, The Causes for Variations in. S. W. Parr ... 352

WASH Bottle, A Self-Filling Measuring. O. C. Smith ... 905
Water Bath, Unique. S. W. Wiley ... 454
Water, Boiler-Feed, The Purification of. W. A. Hamor ... 851
Water Conservation Exhibit, Municipal, of the City of Philadelphia. A Note 778
Water, Drinking, A Simple Method for Purifying. J. L. Sammis 681
Water Flow Recorder, A. W. A. Hamor 688
Water-Gauge Glasses. W. A. Hamor ... 461
Water, Purification of, by Forced Oxidation. W. A. Hamor ... 384
Water Purification Process, The "Chloride." W. A. Hamor ... 385
Waters, The Disinfection of Potable, by Chloride of Lime. Editorial W. A. Hamor 777
Waters, The Sterilization of Potable. W. A. Hamor 461
Water Tester, The Digby and Biggs Dionic. W. A. Hamor ... 386
Water, The Purification and Softening of, by Permutite. Editorial W. A. Hamor 240
Whale, Epinephrin from the. E. R. Weidlein ... 636
Wheat, Irrigated and Dry-farming, Comparative Value of, for Flour Production. R. Stewart and C. T. Hirst ... 270
Wheat Flour, Acidity in, Its Relation to Phosphorus and to other Constituents. C. O. Swanson ... 274
White Lead, The Manufacture of. W. A. Hamor 462
Wine Industry, Argentina's. Consular Note ... 232
Wood, Distillation of Resinous, by Saturated Steam. L. F. Hawley and R. C. Palmer ... 789
Wood Distillation, Some Recent Developments in. T. W. Pritchard 338
Wood Preservative, A New. W. A. Hamor ... 774
Wood Preserving. W. A. Hamor ... 385
Wood Preserving Oils, The Value of the Higher Phenols in. S. Cabot 206
Wood, The Phenomenon of the Apparent Disappearance of the Higher Boiling Phenols in Creosoted, and its Explanation. S. Cabot 266
Wood, The Preservation of, with "Bellit." W. A. Hamor ... 542

ZINC, Bibliography on Methods of Estimation of, 1890–1911. Report of Committee on Quantitative Methods. F. O. Taylor ... 468
Zinc, Electrolytic Recovery of. Consular Note ... 231
Zinc Losses. Mineral Wastes Symposium. W. H. Bassett ... 164
Zinc, The Determination of, by Electroanalysis. E. B. Spear and S. S. Strahan ... 889

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